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BATTELLE REMORIAL INSTITUTE

AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS FOR PROTECTION OF STEEL AIRCRAFT PARTS

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FORE ORD

This report was prepared by the Battelle Memorial Institute under Contract No. AF 33 (038) 8750 identified by Research and Development Order No. 611-11. "Electrodeposition and Electrochemical Treatments." It was administered under the direction of the Materials Imporatory, Directorate of Research, Wright Air Development Center, with Mr. C. B. Foertmeyer acting as project engineer. The report is one of a series to be published on the project as research progresses. The materials work covered by dates form 5 Nov 1985.



ABSTRACT

Work done in this report covers the preparation and evaluation of eleven allow deposits. Methods and solutions used for the preparation of both co-deposits and diffused coatings are listed. Results of "Wet-Dry" exposure tests, x-r y diffraction, potential - time data of various coatings have been tabulated. A graphical system for the better interpretation and rating of the "Wet-Dry" test was det loped. Marganese-zinc alloy diffusion type coatings of 50% mangarese and 50% zinc composition exhibited the most promising corrosion protection properties of the various coatings investigated. Seventy-two panels were prepared and are being tested in outdoor exposure in northern Florida in order to evaluate the corrosion protection afforded by mangarese and mangaresezine coatings as compared to zine, zire chromated, and cadmium coatings It is believed that a co-deposited zinc-silver coating of 25% silver merits further investigation. Also further studies of corrosion products should yield information enabling the design of an alloy coating of maximum protection.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

M. F. SORTE Colonel, USAF

Chief, Materials Laboratory

Directorate of Research

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OBJECTIVES FOR THE PROJECT

The ultimate objective is to develop electrodeposited coatings which will provide better protection for strongft steel parts than does zinc or cadmium plate, particularly in tropical regions.

Two years have been spent in partial attainment of this objective, and the results have been reported. (See Final Report, dated November 30, 1947, and Final Report, dated June 28, 1949).

Under the present contract, the objectives were:

- (1) Continuation of work on zinc-silver, zinc-lead, and zinc-tin alloy platings.
- (2) Measurement of electrode potentials of manganese—tin, manganese—zinc, and manganese—copper alloys in 3% sodium chloride solution, distilled water, and CO2—saturated water. This assumed that the alloys would be electromeposited. Any of the alloys showing favorable potentials were to be exposed in the "wet—dry" cabinet. (The manganese—nickel system is also included here, insofar as the plating investigation is concerned. Potential measurements on cast manganese—nickel alloys had been completed.)
- (3) Investigation of methods for obtaining good adhesion of aluminum deposits on steel, using aluminum-plating methods which had already been developed.
- (h) Investigation of methods for depositing zinc-chromium, cadmium-chromium, and cadmium-manganese alloys. Those which could be deposited and show favorable potentials were to be exposed in the "wet-dry" test.
- (5) Outdoor exposure of alloy coatings which show good corrector resistance in the preliminary tests. This was to be done at the Battelle North Florida Research Exposure Station, if, and as, time permitted during the contract period.

(6) Investigation of other pure metals or alloys showing promise as substitutes for zinc and cadmium. The only metal in this catagory is molybdenum. Its potential is such that it would have to be alloyed with zinc, cadmium, or manganese.

INTRODUCTION

The experimental approach used in attaining the foregoing objectives was somewhat different than visualized for the project at the start.

After a time it became apparent that codeposition studies were consuming too much time in proportion to the benefits derived, and that preparation of alloy coatings on steel would probably be expedited by using diffusion methods. For this reason, much of the effort was centered on obtaining alloy coatings by diffusion heat treatments of alternate layers of pure-metal plates.

Less emphasis was placed on potential measurements. Where the coatings were readily prepared, it was thought better to test them immediately in the "wet-dry" cabinet. Potential and current-density measurements were used extensively during the first and second years of work and were useful in separating good prospects from the poor ones. It will be recalled, however, that in the early work, cast alloy specimens, rather than coatings, were used.

Hethods for depositing aluminum from nonaqueous organic solutions were developed here on a project sponsored by the Navy. A

study of methods for improving the adhesion of aluminum to steel was planned. This study was contingent upon the Navy's continuing the project, but the project was closed. The amount of effort for continuing the work under this project would have been greater than that allotted in view of the other lines of investigation that had to be carried on.

For this reason, the investigation of aluminum plate adherence was not begun.

This report is a Final Report in the sense that it represents the completion of a phase of an overall investigation. The work to be accomplished during this phase was set forth in the contract which authorized this project. Recently a supplemental contract has been entered into, which authorizes outdoor testing of protective coatings described later in this report, and an investigation of methods for electrodeposition of certain binary manganese alloys.

RESULTS ACCOMPLISHED

An alloy coating containing 50% manganese and 50% zinc zhows promise as a protective material for steel*. This alloy is superior to pure zinc as a protective coating when exposed in the "wet-dry" cabinet**. The coating was prepared by heat treating a duplex coating of manganese and zinc electroplates so as to cause interdiffusion. The alloy has an advantage over pure manganese in that the corrosion products appear to be less bulky and are more adherent.

Most plated panels discussed herein had an S.A.E. 4130 steel basis for plating, as shown in Appendix I.

See Appendix I for description.

hanganese and tin were codeposited from a tartrate-oxalate bath, but the reproducibility in plate composition was poor. The study of manganese-tin alloys containing 40% to 50% manganese was continued with diffusion coatings. These alloys showed better inherent corrosion resistance than pure manganese, since the characteristic brown corrosion products developed more slowly on the alloy, Pure manganese gave a higher degree of sacrificial protection.

A peculiar phenomenon was observed with the manganese-tin diffusion alloys. After standing at room temperature for five or more days, a gray powder formed on the surface. X-ray diffraction tests showed that the powder was tin, but not gray tin. No explanation was found for this apparent "disintegration" of the diffusion alloy.

Attempts were made to prepare a sound codeposit of zinc and silver, first using an iodide solution, and second using a thiosulfate solution. Both zinc and silver were found in the deposit which was powdery and nonadherent.

zinc-silver alloy coatings prepared by diffusion showed extremely poor resistance in the "wet-dry" test. This is thought to be due to a small amount of free silver in the coating. It is believed that, if the coating can be prepared so as to eliminate the free silver, a resistant coating will result in accordance with expectations from the potential measurements and weight-loss measurements on cast zinc-silver alloys.

Codeposits of manganese and nickel were obtained from solutions containing ammonium salts. The manganese content was very low, however.

Some evidence of diffusion was found after heat treating manganese and nickel duplex plates. After a twenty-one-hour heat treatment, the identification of pure nickel and pure manganese was questionable and a strong pattern of iron and an unknown phase: ... found.

Slight evidence of the interdiffusion of zinc and chromium electroplates was found. The only X-ray data available were obtained here from some low-chromium castings. The lack of complete X-ray data was a handicap.

No interdiffusion was detected of cadmium and chromium or of manganese and cadmium electroplates.

No work was done on manganese-copper alloys, because it had been mutually agreed to defer this until the Navy tests on the same subject were complete.

Work supported at Battelle by the Tin Research Institute, Inc., overcame previous difficulties with zinc-tin alloy plating. Revised directions for using the zinc-tin bath are given in Appendix I.

Experiments on the codeposition of zinc and lead resulted in nonadherent, coarsely crystalline deposits containing mostly lead.

Zinc-nickel-coated ("corronized") 4130 steel panels were exposed in the "wet-dry" test, in which they rusted fairly rapidly. As the nickel content increased from 25% to 50%, the advance of rusting became slower.

Cadmium-tin diffusion coatings, and also cadmium-tin codeposited coatings (both types containing about 50% cadmium) were exposed in the "wet-dry" cabinet. These coatings are comparable to pure cadmium coatings, with the codeposited alloy being somewhat better.

Cadmium-silver codeposited coatings rusted early in the "wet-dry" test, but subsequent rusting progressed slowly. This alloy was slightly inferior to pure cadmium in the "wet-dry" test. Jeight-loss measurements on cast cadmium-silver specimens, after exposure in the "wet-dry" test, showed the alloy to have about the same resistance as pure cadmium.

Although one of the requisites for a substitute coating was that it give sacrificial protection, some thought was given to the non-sacrificial type of coating. An iron-chromium alloy containing 6% iron has been developed here (under a separate government sponsorship).

The alloy plate does not have the usual cracks associated with chromium deposits. Because the coating could conceivably give envelope—type protection, it was tested in the "wet-dry" cabinet. The iron-chromium alloy, however, was no better than the chromium-plated panels which were exposed at the same time.

The effect of light nitriding of the steel surface prior to pure zinc plating was studied. The nitrided panels showed no significant improvement over the unnitrided panels.

A proposed graphical system for rating coatings after exposure in the "wet-dry" test is described. The method involves a graphical integration of time and extent of corrosion. It represents a first attempt to obtain a single number which describes the relative corrosion resistance.

The manganese-zinc corrosion products were studied by means of X-ray diffraction. Only manganese oxides were detected. The type of oxide appears to be related to the composition of the alloy.

Seventy-two coated 4130 steel panels, for outdoor exposure at the Battelle North Florada Research Station, were prepared. Pure manganese, manganese-zinc, and zinc-tin coatings will be tested in comparison with pure zinc, zinc plus chromate, and pure cadmium. Three thicknesses, 0.1 mil, 0.3 mil, and 0.5 mil, were prepared for each type of coating.

DISCUSSION OF ESSENTIAL DATA

Zinc-Silver Alloy Coatings

Introduction

Measurement of dynamic potentials and corrosion-current density of cast alloys previously had shown that a zinc-silver alloy containing 25% silver held promise for improved corrosion resistance in comparison with pure zinc. (See Final Report, dated June 28, 1949.)

This was further substantiated by weight-loss measurements on cast alloy specimens exposed in the "wet-dry" cabinet. The 25% silver alloy lost less weight in the test than either zinc or cadmium. (See Final Report, dated June 28, 1949.) Experiments were then started on the preparation of alloy coatings by electrodeposition.

Experiments on the Codeposition of Zinc and Silver

These experiments were started during the second year of work on this project. According to calculations (see Final Report dated June 23, 1949), the deposition potentials of zinc and silver could be brought closer together by complexing the silver as a complex iodide.

This would reduce the silver ion concentration, making its deposition potential more negative. By using a high concentration of zinc iodide (which does not form a complex in iodide solutions), the zinc deposition potential would become somewhat more positive.

Potential measurements in solutions containing the single ions, zinc or silver, demonstrated that such a change took place. Even with the small amount of polarization, due to passage of current, the deposition potentials were not close enough so that codeposition could be predicted.

When the ions were present in the same solution, codeposition did occur, possibly indicating increased polarization of the silver.

The codeposition experiments are described in Table 20, Appendix I.

In general, the codeposits from the iodide solutions were characterized by a rough and powdery surface. The deposits were not rough from the very beginning. A thin flash-plate was obtained before the roughness would begin. Raub and "ulhorst", using a cyanide solution, and Wood and Saunders**, using a cyanide-hydrazide solution, also were able to get only flash plates, followed by increasing roughness.

A number of additional agents were tried without improving the deposit. (See Table 20, Appendix I.)

The convention as to the sign of the potential is the one adopted by the Electrochemical Society, where the active end of the electromotive-force series is negative.

^{**}Metallforschung 2, 33 (1947).

^{***}

[&]quot;A Study of Silver-Zinc Coatings for Steel Flatware", Report to War Metallurgy Board, March 1, 1943.

The first experiments were run at 85°F. Increasing the temperature to 177°F. caused the deposit to become worse. Lowering the temperature to 40°F. seemed to improve the deposits, but they still were not acceptable as coatings.

The plate composition is quite sensitive to current density.

Figure 1 shows this relationship.

The powdery deposits were at first believed due to a silver immersion plate which formed after the initial deposit of alloy. The alloy, being more active than silver, displaces silver from the solution. This view has been discarded and for reasons discussed later in this section.

Because of the thought that immersion plating was responsible for the poor deposits. new complexing agents were sought.

The first of these was the silver ethylene thiourea complex.

The complex is easily formed from ethylene thiourea and silver nitrate.

It is soluble in water and silver deposits were obtained at 15 amps./sq.ft.

and 80%. Static-potential measurements in this solution resulted in

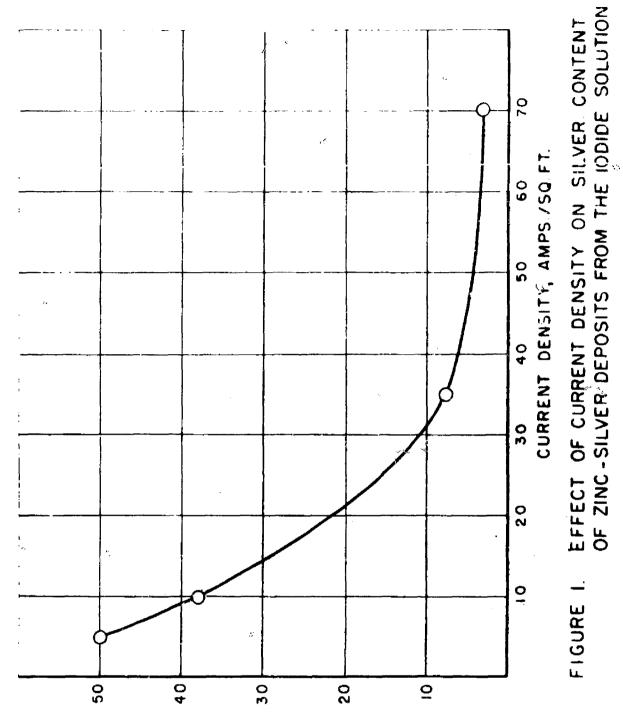
values about 200 millivolts more electropositive than those in iodide

solutions. This indicated that the silver was not complexed enough to

obtain the desired shift in deposition potential.

Pyridine showed insufficient power as a complexing agent. Silver in pyridine was oxidized to a divalent form by persulfate, but this complex was also weak, the silver being displaced easily.

During an investigation for another sponsor, it was found that, if a solution of silver nitrate in dry acetonitrile was treated with dry ammonia gas, a precipitate formed which was presumably a silver



SILVER CONTENT, PER CENT BY WEIGHT

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10

complex. The solution was then saturated with respect to this silver complex. Zinc did not displace silver from such a solution as long as no water was present. A deposit of black colloidal silver was obtained on passage of a current. This solution did not appear to hold practical possibilities and the investigation was discontinued.

Static-potential measurements on the silver thiosulfate complex indicated it to be only slightly less favorable than the iodide complex, being 20 millivolts less negative. With a current of one amp./sq.ft., silver sulfide was produced at the cathode and the cathode-potential value changed from -O. I. II. volts to -1.10 volts. This large change in potential resulted from the great reduction of silver ions adjacent to the cathode when the silver precipitated as Ag₂S (the equilibrium constant for Ag₂S is 1.0 x 10-51). A study of the literature revealed that if certain precautions were taken the precipitation could be avoided. Hickman*, et al., defined the conditions.

Hickman recommended that the solution be acidic, that sulfite and gelation be present, and that rapid agitation be used. The directions were followed in solutions containing both zinc and silver. Spongy nonadherent deposits containing both silver and zinc resulted. Sulfur was also found in the deposit, although less of it deposits if gelatin is present.

During these experiments, silver was easily displaced by a more active metal, such as zinc, from a thiosulfate complex, but if zinc is present no displacement occurred. On electrolyzing the solution, an unsatisfactory deposit resulted. This east doubt on the earlier

^{*}Ind. Eng. Chem., 25, 202 (1933).

observation that the poor zinc-silver deposits were probably caused by a simultaneous immersion deposit. Another factor which made the immersion theory untenable is that increasing the current density aid not improve the deposits.

Because of time limitations and the desirability of producing a satisfactory rinc-silver alloy coating within the contract period, the sedeposition work was discontinued in favor of preparation by diffusion. This decision applied not only to the sinc-silver alloys, but wherever this method of preparation was practicable and could save time in studying other alloy coatings.

Experiments on Zinc-Silver Alloy Coatings by Diffusion

In general, the preparation of alloy coatings by diffusion consisted of plating Metal A on the steel panels, plating Metal B over Metal A, thus forming a duplex plate, and then heating them to a sufficently high temperature—that interdiffusion occurred. The alloy composition was controlled by the relative amounts of A and B which were deposited. The heat treating can be done in an inert-gas atmosphere, in air, or in an oil bath. The choice depended on the temperature and the chemical properties of the metals.

The initial experiments with duplex plates of zinc and silver disclosed that interdiffusion of zinc and silver took place at 700°F., in a purified-nitrogen atmosphere to prevent exidation. The extent of diffusion was determined, in these early experiments, by microexamination. Subsequent use of X-ray diffraction for examination of the diffusion

specimens expedited the work, because relatively thin coatings could be used (0.3 mil, as compared with 2 to 4 mils for microexamination), and the specimens required no special preparation, such as was necessary for microexamination. Experiments with duplex plates with a total thickness of 0.3 mil demonstrated that diffusion could be brought about in one hour at 500 T.

At first it appeared best, in preparing the duplex deposits, to plate the silver directly on the steel and then zinc plate. Silver does not diffuse into steel at temperatures (500°F.-800°F.) which cause interdiffusion of zinc and silver. There was a possibility that zinc would, if deposited first, diffuse into the steel. Thus, a zinc-silver alloy coating low in zinc would result. If sufficient zinc was "robbed" by the steel, the coating might not provide sacrificial protection for the steel.

However, when silver was plated directly on the steel (using a single strike solution and a regular plating bath, but no special pretreatment), it blistered during heat treatment. Therefore, duplex coatings were prepared with the sinc next to the steel. The total thickness was 0.0003 inch (the thickness previously chosen as standard for the "wet-dry" exposure test), and the respective weights were such as to give a resultant alloy of 25% silver content. The coatings were heat treated in a purified-nitrogen atmosphere for one hour at 500°F.

Observation of the coatings, following heat treatment, showed them to have changed in color from silvery white to a blue gray. This alone was indicative of diffusion having taken place. The coating was wrinkled along the edges of the specimens but no breaks were apparent.

X-ray diffraction measurements showed the desired epsilon phase (see constitution diagram, p. 1155, American Society for Metals Handbook, 1943) to be present and also a small amount of free silver (estimated to be, at most, a few per cent).

The static potential of one of the specimens was measured in three per cent sodium chloride solution. The values are given in Table 1. The results show that diffusion took place. If diffusion had not taken place or had been incomplete, the potentials would have been more electropositive.

The value for 60 minutes is some hundred millivolts more negative than that for the cast alloys of the same composition. (See Final Report dated November 30, 1947, p. 45.) At 120 minutes and beyond, the potential is equal to that of the cast alloy.

After 330 minutes in the salt solution, the panel showed only a trace of corrosion products. The coating flaked at the edges, and beneath it was observed a thin silver-like layer so that the steel was not exposed. This may be a silver or silver-rich layer, but the reason for its being found on the steel is unknown. X-ray diffraction measurements detected a small amount of zinc-iron alloy in one of the specimens where the zinc was plated first. This was undesirable for reasons stated above.

The remaining alternative was to plate the silver on the steel first, so the problem of producing adherent silver deposits directly on S.A.E. 4130 steel was taken up once more. Success came easily. U.S. Patent 2,431,947 described an anodic treatment in phosphoric acid solution which purportedly caused a strong bond to be formed between the

TABLE 1. POTENTIAL-TIME DATA FOR ZINC-SILVER DIFFUSION ALLOY (No. 4557-56A), CONTAINING 25 PER CENT SILVER, IN THREE PER CENT SODIUM CHLORIDE SOLUTION AT 90°F., SATURATED-CALONEL SCALE. VALUES IN VOLTS.

Elapsed Time (Mins.)	Potential	Elapsed Time (wins.)	Potential Potential	-
<i>y</i> 1	-1.012	120	-0.911	
10	-1.023	150	-0.914 &	
20	-1.027	180	-0.922	\$
30	-1.030	210	-0.919	
40	-1.030	300	-0.912	
50	-1.031	33 0	-0.913	
60	-1.030	•		. -

steel and silver. A trial of the method showed the claims to be valid.

The anodic treatment etched the steel uniformly, leaving a carbon smut on the surface, which was easily removed by brushing in a stream of tap water. The adherence of the silver was tested by heating the specimens at 500°F. for an hour. No separation of the silver from the steel occurred. Previously, electropolishing had been tried as a pretreatment, but the silver did not adhere. Apparently, a satisfactory mechanical hond is formed with the stehed surface. Details of the anodic treatment are given in Appendix I.

A series of panels was prepared with a 0.0003-inch-thick zingsilver diffusion allow containing approximately 25% silver. Details
of the electrodeposition are given in the experimental section and in
Appendix I.

The X-ray results and the heat-treating data are given in Table 2. Characteristic photograms for each type of costing are shown in Figure 8*, Appendix II. Specimens 63A, 65A, and 72A showed the epsilon phase and silver to be present as given in photogram type 3, Figure 8. Free silver was estimated as being present to the extent of 2 to 3%. The necessary data for phase identification have been worked out by Gwen and Pickup**. The epsilon phase has a hexagonal close-packed structure with a range in a from 2.81 to 2.82 Å, and c varies from 4.35 to 4.47 Å as the silver content varies from 20 to 46 weight per cent. The cell dimensions of the compound identified in these three specimens correspond to an alloy containing between 20 and 30%

silver.

[&]quot;The relative intensities in Figure 8 are estimated relative intensities for each photogram (with an exception), but can not be carried from one to another. The exception is the photogram for the zinc-silver epsilon phase. Here the relative intensities are represented as all being equal, because no intensity data were available.

Proc. Roy. Soc., н. 140, 344 (1933).

A-RAY DIFFRACTION STUDIES OF ZING-GILVER DIFFUSION ALLOY COATINGS, AND ZING ON STENE :\ABI& 2.

the common the part of

-654 75 m - 25 4g 500*7, 1 hr., 2n first bymilom(1) phase + 4g(2) See Figure 8, photogram Type 8, 1 at all 200*7, 2 hrs., 2n first bitto b	Specimen Number	Pur Cent Composition of Costing	Conditions for Diffusion	Order of Deposition	Phases Present by X-Ray Diffraction	Remarka
Ditto 4.00°F., 2 hrs., 2n first Ditto 1 Ditto Do * Eu * extra line A 2.27A Pure aina 500°F., 1 hr., 82 atmosphere Ditto Ditto - 2ina * iron Coating two thick, with dilute BGL. Pure aina Bitto - 2ina * iron coating two thick, with dilute BGL. Pure aina Bitto - 2ina * iron coating two thick, with dilute BGL. Pure aina Bitto - 2ina * iron coating two thick, at first aina a stransphere at a 2ina * iron coating two thick. 75 in - 25 Ag 500°F., 1 hr., Ag first Epsilon phase • Ag 75 in - 25 Ag 250°F., 6 hrs., Ag first Epsilon phase • Ag 75 in - 25 Ag 250°F., 6 hrs., Ag first Epsilon phase • Ag 75 in - 25 Ag 250°F., 6 hrs., Ag first Ag 75 in - 25 Ag 250°F., 6 hrs., Ag first Epsilon phase • Ag 75 in - 25 Ag 250°F., 6 hrs., Ag first Ag 250°F.	جً - 634	75 Sa - 25 Ag	500°F., 1 hr., N., atmosphere	Zn first	Spation(1) phase + Ag(2)	See Figure 8, photogram Type B.
Pure zing S00er, 1 hr., 21nc 21nc 21nc 21nc 21nc 21nc 21nc 21nc	¥\$9-	Ditto	400°F., 2 hrs., oil	Zn first	Ditto	
Pure zine 500°F., 1 hr., - Zinc + iron Coating two thick. Ditto Ditto - Zinc + iron coating two thick. Pure zine 500°F., 1 hr., - Zine + iron diffue BCI. Ditto Ditto - Zine + iron coating two thick. Ditto Ditto - Zine + iron coating two thick. Ditto Ditto - Zine + iron coating two thick. This was 'num as a st Ag first Epsilon phase - Ag No 250°F., 6 hre., Ag first Epsilon phase - Ag No 250°F., 6 hre., Ag first Ag - Zine	₩\$9-	E		Ditto	Do + Zu + extra line at 2.27A	X-ray bean on thin place on sample.
Pure zine 500°F, 1 hr., — Zine * iron Goating two thick. But zine 500°F, 1 hr., — Zine * iron Goating two thick. But atmosphere 75 in - 25 Ag 500°F, 1 hr., Ag first, Epsilon phase • Ag 75 in - 25 Ag 250°F, 6 hre., Ag first Ag • Zine • Zine • Jun as a st Ag 250°F, 6 hre., Ag first Ag • Zine • Jun as a st Ag • Zine • Jun as a st Ag 250°F, 6 hre., Ag first Ag • Zine • Jun as a st Ag • Zine • Jun as a st Ag 250°F, 6 hre., Ag first Ag • Zine • Jun as a st Ag • Zine • Zine • Jun as a st Ag • Zine • Zine • Jun as a st Ag • Zine • Zine • Jun as a st Ag • Zine • Jun as a st Ag • Zine • Jun as a st Ag • Zine • Zine • Jun as a st Ag • Zine • Zine • Jun as a st Ag • Zine • Zine • Zine • Zine • Jun as a st Ag • Zine • Z	₩59.·	Pure aind	500°F., 1 hr.,	•	2,106	
Pure zino 500°F., 1 hr., Butto Ditto — Zing + iron Pure zine Bo diffusion — Zing + iron 75 Zin - 25 Ag 500°F., 1 hr., N2 stmosphere 75 Zin - 25 Ag 250°F., 6 hrs., Ag first Epsiloa phase • Ag 250°F., 6 hrs., Ag first Ag 250°F., 6 hrs., Ag first Ag 250°F.	459-	Ditto	Ditto	1	Zine + iron	Coating two thick. Part of it was etched off with dilute BCL.
Pur sinc No diffusion - Zing + iron Pur sinc No diffusion - Zing + iron 75 2n - 25 4g 500 - 1 hf., Ag first, Epsilon phase • Ag 75 2n - 25 Ag 250 - F., 6 hfs., Ag first Epsilos phase • Ag 75 2n - 25 Ag 250 - F., 6 hfs., Ag first Epsilos phase • Ag 75 2n - 25 Ag 250 - F., 6 hfs., Ag first Epsilos phase • Ag • Zn	E69-	Pure zino	500°F., 1 hr., N2 atmosphere	1	21ne	
Pure sine No diffusion - 25 Ag 500°F., 1 hf., Ag first, Epsilon phase • Ag N2 atmosphere 75 2n - 25 Ag 250°F., 6 hrs., Ag first Epsilos phase • Oil Ag 250°F.	869°	Ditto	Ditto	•		Coating teo thid: Part of it was atched off with dilute HG1.
75 In - 25 Ag 500°F., I hr., Ag first, N2 stmosphere 75 In - 25 Ag 250°F., 6 hrs., Ag first, oil	269-	Pure sine	No diffusion	•	21110	This was fun as a standard.
75 2n - 25 Ag 250°F., 6 hru., Ag first oil	-72A	75 2in - 25 Ag	500°F., 1 hr., N2 stmosphere	Ag filst	Epsilon phase * Ag	
	-73A	75 2n - 25 Ag	250°F., 6 hFE.,	Age fires	Epsiloa phase +	

Phase nomenclature according to constitution diagram page 1155, ASM Metal Handbook, 1948 Edition. Estimated to be 2 to 3 per cent by weight. 3

^(~)

Specimen 65A, which was heated in mineral oil at 100°F. for 2 hours, showed some free zinc at one location on the sample (see photogram type A, Figure 8, Appendix II). No explanation is known for the fact that 65A had free zinc in one place and not another. The presence of an extra line at 2.27Å might be attributed to the existence in this sample of a range of composition is epsilon phase. Specimen 73A, which was heated at 250°F. in oil for six hours, also had some free zinc (see photogram type A, Figure 8, Appendix II). These temperatures are probably too low. No experiments were conducted at higher temperatures in oil because the mineral oil had a flash point of 1440°F.

During the time that these experiments were being carried on, a separate investigation was made to establish beyond doubt whether zinc and iron do interdiffuse at 500°F. Two S.A.E. 4130 steel panels were plated with 0.0003 inch of zinc. These were heated at 500°F. for one hour in a purified-nitrogen atmosphere. It was necessary to dissolve some of the coating off because the zinc pattern might have overshadowed the sinc-iron alloy lines, if any. No evidence of the interdiffusion of zinc and iron was found. Zinc was plated first in some of the subsequent tests, whereas silver was plated first in others.

In preparing specimens to be used for "wet-dry" exposure, diffusion was effected at 500°F. for one hour in a purified-nitrogen atmosphere.

The first signs of rust were observed on the zinc-silver coatings after four cycles in the "wet-dry" cabinet. The advance of rusting was very rapid. Two specimens which had been plated first with zinc were

heat treated in the same way and exposed in the "wet-dry" cabinet. These failed about as rapidly as the first group. These results are tabulated in Table 25, Appendix I.

The rapid deterioration of the diffusion-formed, zinc-silveralloy coatings was unexpected, in view of the insignificant weight
losses incurred by the cast specimens containing 25 per cent silver. (See
Final Report, dated June 28, 1949.) What, if any, was the difference in
the two alloys?

Two of the cast specimens from the early work were X-rayed. Pure epsilon phase (AgZn3) was found with no trace of free silver. A small amount (3 to 5 per cent) of free silver was always found in the diffusion coatings that failed. Thus, with free silver, the potential relationships are favorable for rapid corrosion. The AgZn3 has a potential about equal to that of zinc, while the potential for silver is more noble by over a volt. The results of the X-ray diffraction studies are given in Table 3, and typical photograms are given in Figure 9, Appendix II. When 3-1/2 hours of additional heat treatment was given to Specimen 4557-72A, the identification of the free silver was questionable. Specimen 4557-98A, which was heated for eight hours at the same 500°F. temperature, failed to show any free silver, (Standard Ag2n; photogram, Figure 9.) The high-purity nitrogen that was used as an atagephere during the heat treating contained small amounts of oxygen, which account for the presence of zinc oxide (Standard 2n0 photogram, Figure 9, Appendix II).

In accomplishing the apparent solution of the silver, an undesirable condition was created. The coatings flaked from Specimens 4557-98% and 4557-98%, the latter being the more serious. A loose

TABLE 3. DESCRIPTION OF ZINC-SILVER DIFFUSION COATINGS AND RESULTS OF X-RAY DIFFRACTION EXAMINATION

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Andrew Standard Company of the Compa				ć::=	
Specimen Number	Composition (Weight S)	Conditions For Diffusion	Order of Deposition	Remarks	Phases Identified by I-Ray Diffesciion
2375-62D1	24.8% Ag		į	Cast-alloy spectrometer record.	S-kgZng (epsilon)
-6203	Ditto	i	1	Ditto	S-4.8233
-6201	=		=	Filings. Powder photogram.	S. A. [23]
4557-72A	23% Ag	1 Hr., 500°F.	Ag Pirat	1	S-4gZn3 + VF-4g
		3-1/2 Hrs., 500°F.	}	. 5.	9-4gZn3 + Ag(7)
				Abraded lightly.	8-4g2n3 + Ag(7)
		h	•	More abresion.	8-14 + u284.8
4557-984	28% AB	8 Hrs., 500°F.	Zn Pirst	Coating flaked.	S Ag2n3
		•	÷.	Loose flake from -98A.	3-Ag223 + F-ZD
:557-98B	23.6% Ag	1 Hr., 500°F.		S .	;
-		1 Hr., 700°F. +			
		2 Hrs., 800°F.	Zn First	Coating flaked wore than 4557-484.	S-&gZn3 + P.Zn + P-2n3
				Steel surface after removal of loose flake.	**************************************

The letters S, MS, M, F, and VF refer to the relative intensities (strong, medium strong, medium, faint, and very faint) of that phase's diffraction pattern.

X phase has not been positively identified, but it may be an Fe-Zm alloy.

*

flake from -98A had a small amount of free zinc. Free zinc probably would not be harmful, because the AgZn₃ has about the same potential as pure zinc.

Successive abrasions of Specimen 4557-98A showed that the AgZn₃ existed throughout the entire thickness of the conting. A private communication, received from the Standard Steel Spring Company, revealed that flaking was always associated with zinc deposited from a cyanide solution. They developed a special acid solution* which prevented flaking. It was also learned that, in the preparation of the zinc-nickel ("corronized") costings, the nickel is deposited first and is covered with the zinc. Heat treating is done in air at 700°F., and diffusion is reported to be complete in thirty minutes. No visible exidation takes place, but the resulting coating is a dark blue-gray in color.

Taking a cue from that work, an experiment was performed to see if the acid sinc solution would be effective in preventing flaking of zinc-silver coatings. Two sets of four specimens each were prepared with duplex zinc-silver coatings. These are the first eight specimens in Table 4. In all cases, the zinc was deposited first. Four specimens received zinc coatings from the cyanida solution, and the remaining four were coated in the special acid solution. All eight were silver plated in the same way. The two sets were heat treated simultaneously in air at 600°F. At the end of one, two, four, and eight hours, one specimen from each set was removed from the furnace. No flaking was observed in the "acid" specimens, but the "cyanide" specimens showed flaking. The acid specimens had a pour appearance, however.

^{*}The composition of the special acid-type solution is not given in this report because no permission has been granted to do so.

TABLE 4.0 DESCRIPTION OF ZINC-SILVER DIFFUSION COATINGS AND RESULTS OF 1-PAY DIFFRACTION EXAMINATION

Junga 2

Specimen	Composition (Welcht \$)	Order of Deposition	Type Bath For Zinc Deposition	Conditions For Diffusion	Remerks	10 N	. Phases Identified by X-Ray Diffraction*
1,557-98H	25.2% AB	Zinc First	Cyanide	1 Hour, 600°F., Air	ir Blue-gray color. Coating peeled.	Coating peeled.	S-Ag2n, + VP-Ag
186-	22.2% A.B	Ditto	Ditto	2 Hours, 600°F., Air		3	S-A (Zn + VP-Ag
8 8	22.1% Ag	E	ε	4 Hours, 600°F., Air	Air		S-A 3Zn + VP-Ag
-98r	23.8% AR	£		8 Hours, 600°F., Air	41.	• •	3-48Zn + 7/F-Zn0
5327-35B	24.5% 18		Acid	1 Hour, 600°F., Air	r Mottled color. No peeling.	peeling.	S-A(25) + M-Ag
-350	23.5% Ag		*	2 Hours, 600°F., Alr	Alr Ditto	q	S-A/221 + 105-Ag
-354	25.0% AR	£		4 Hours, 600 F., Air	Air	•	S-4×2Zn + W-4x
-350	25.0% Ag	=	£	8 Hours, 600°F., Afr	Afr		3-4(2)3 + MP-40
5327-433	214.0% Ag**	Silver First	e	1 Hour, 600°F., Air	ir Lustrous mat. No peeling.	peeling.	S-4EZ33. + VF-42
⊃ €11 -	24.0% Age*	Ditto	£	2 Hours, 600°F., Air		q	S-48211 + VF-48
-435	24.0% Ap#	=	.	4 Hours, 600°F., Air	Air "		S-A97.11 + 1-10
-1,3E	214.0% Agr	=	=	8 Hours, 600°F., Air	Mr		S-8 - 2 - 2 - S

The letters S. 15, M. F. VF, and VVF refer to the relative intensities (strong, medium strong, medium, faint, very faint, and very, faint, and very faint, and #

** Nominal.

Previous results had shown that, after eight hours of heat treating, no free silver could be detected by X-ray diffraction.

Table 4 shows that free silver may be present in spite of the longer heat treatment. Also, the fact that no silver is detected by X-ray diffraction is no assurance that very small amounts are not present.

The experiment was repeated with the silver being deposited first, and only the acid zinc solution was used. The resultant coatings showed no flaking. They had lustrous, mat surfaces; in fact, they looked better after heat treating than before. These specimens were exposed in the "wet-dry" cabinet and failed after only one cycle. No difference due to heat-treating time was observed.

The methods for plating the duplex specimens are described in Appendix I_{\bullet}

Apparently, the preparation of resistant zinc-silver coatings by diffusion is not practicable or will involve a longer research before success is attained. It may be that, in order to achieve a satisfactory coating, codeposition studies will have to be resumed.

The influence of the heat-treating atmosphere on the zinc-silver coatings was tested by diffusing several duplex-coated specimens in hydrogen. Then exposed in the "wet-dry" cabinet, these specimens rusted as rapidly as those heat treated in air (two cycles). Two specimens, coated with a zinc-silver duplex, undiffused plate, were also exposed. They showed rusting after two cycles, also.

Duplex plates, such as these with the zinc on the outside, would be expected to protect steel longer than for two cycles. The zinc made up more than 0.2 mil of the total coating thickness (0.3 mil). A simple zinc coating of 0.2-mil thickness on steel would prevent rusting for a longer period. The free silver is then probably the cause for the rapid rusting. Whereas the test with duplex plates does not prove the belief, it does support the idea.

The possibility of the coating being porous was eliminated by testing electrographically. No pores were detected.

Tests on Galvanic Couples Formed From Aluminum and Zinc-Silver Alloys

There is a possible danger in the use of alloy coatings which contain noble metals for protecting steel parts of aircraft. If the corrosion products from the alloy come in contact with aluminum or its alloys, the noble metal might deposit (by chemical displacement) on the aluminum. Thus, a couple would be formed in which the aluminum would be anodic, and as such would corrode rather rapidly. Alloys containing copper, such as brass, are "bad actors" in this respect.

The above discussion could also apply to zinc-silver alloys, the corrosion products of which might contain small amounts of silver. If a metallic deposit of silver formed on aluminum, the latter might corrode.

To determine the amount of corrosion brought about by such combinations, a group of couples was exposed in the "wet-dry" cabinet.

Two zinc-silver alloys were used, one containing 17 per cent silver, the other 25 per cent silver. Two types of aluminum were used, bare 24ST

and 24ST Alclad. The aluminum specimens measured four inches by one inch, and the zinc-silver alloy pieces were about 3/4 inch square. The zinc-silver alloy specimens were clamped to the aluminum at one end by means of the Lucite washers which support the specimens in the cabinet.

After 150 cycles (75 days), the couples were removed and examined.

The aluminum was lightly corroded all over. There was no evidence of

localized corrosion at the interface between the sluminum and the

sinc-silver alloy, nor elsewhere.

The conditions in the "wet-dry" cabinet might not have been favorable for obtaining galvanic corrosion. The mechanism would require some dissolution of the zinc-silver alloy, with subsequent precipitation of silver on aluminum, thus forming a silver-aluminum couple, in which the aluminum is anodic.

As mentioned above, copper and copper alloys will act in this way so as to produce copper-aluminum couples. As a test of galvanic action in the "wet-dry" cabinet, several couples composed of aluminum and copper and aluminum and brass are now being exposed. The test has not been completed but the results will be communicated at a later date.

Even though the zinc-silver diffusion coatings had little protective value, dropping them from further study is not yet recommended. It is still believed that zinc-silver alloy coatings, if properly prepared, will be protective.

Experiments on the Codeposition of Zinc and Lead

Lead is soluble in zinc to the extent of about one per cent.

Beyond this amount, there is complete immiscibility of the metals at room temperature. Tests made early in this program on cast specimens

disclosed that one per cent lead was insufficient for making a significant improvement in corrosion resistance. An increase is desired in the amount of lead in a zinc-lead alley to be used as a protective coating.

Electrodeposited alloys other than zinc-lead alloys have been prepared which show evidence of greater solubility than would be predicted from the constitution diagram. Electrodeposition, then, is one possibility for making such alloys.

During the first year of work on this project, the codeposition of zinc and lead from cyanide baths, containing tartrate and fluoride, was studied. Wide variations in plate composition were observed even when the plating conditions were apparently identical. No X-ray data were taken, so it is not known what types structure were obtained.

Assuming, however, that no variation from the phase diagram can be expected, a quasi-alloy can be visualized comprising a fine dispersion of lead in zinc. This may also be prepared by electrodeposition.

Attempts to codeposit zinc and lead from fluoborate solutions or zincate-plumbite solutions were unsuccessful. In all cases, lead slone deposited. Examples of these solutions will be found in Appendix I.

This work continued with a study of baths in which the lead exists as a complex chloride. Zinc does not form chloride complexes. In that way, it was hoped to suppress the lead ion concentration, so as to bring the respective deposition potentials close together.

Several lead-complexing agents were tested. What was sought was a lead complex which would have a very low concentration of lead ions

in solution. This would shift the lead potential toward that of zinc if the zinc was not complexed. The static electrode potential of a complex LiCl-PbCl₂ mixture was measured and compared with the potential of a nitrate solution containing the same contentration of lead. The results are given in Table 5. Complexing caused the potential to shift only 200 millivolts in the negative direction. The potential of a one-molal zinc chloride solution would be about -1.0 volt, on the saturated-calomel scale. This leaves a difference of 400 millivolts between the zinc potential and the lead potential in the complex solution. Assuming the respective deposition potentials to be close to these values, considerable polarization would be required, in the case of the lead, in order to have codeposition.

Zinc chloride is even more soluble than lithium chloride.

According to the law of mass action, where the chloride ion concentration
is increased the lead ion concentration will be decreased.

A concentrated zinc chloride solution was made up and a relative—
ly small amount of lead chloride was added to it. Several plating
experiments were made using this complex zinc-lead solution. Table 23,
Appendix I, gives the details of the experiments. The best deposits
were crystalline and treed, with the adherence being poor. Analysis of
the lead in the deposit showed 95 per cent to 97.5 per cent. Since
much higher zinc percentages were desired, it was not thought worth
while to determine zinc except by difference.

TABLE 5. SINGLE ELECTRODE POTENTIALS OF LAAD IN NITRATE SOLUTION AND COMPLEX CHLORIDE SOLUTION. SATURATED-CALOMEL SCALE. VALUES IN VOLTS. 90°F.

Clapsed Time (Mins.)	Nitrate Solution*	Complex Laad Chloride Solution*
3		-0.610
10	- production of the contract o	-0.611
u	-0.411	
21	-0.411	-0.614
35	-0.415	-0.614
58	-0.407	-0.614
110	-0.413	-0.612
193	-0.409	-0,610
360	-0.405	-0.608

Lead nitrate solution contains 41.3 g./1. Pb(NO3)2 or 25.8 g./1.lead.

Complex chloride solution consists of 35 g./l. PbCl2 or 25.8 g./l. lead in a saturated LiCl solution.

Experiments on the Electrodeposition of Zinc-Tin Alloys

The electrodeposition of zinc-tin alloys was investigated by the Tin Research Institute. Their formulation has been used successfully in England in several commercial units. Attempts to duplicate the results at Battelle did not at first meet with success. It was necessary to increase the zinc concentration in order to get the desired plate composition. A study of the problem revealed that high-purity stannate must be used. In England stannate is made from virgin tin. In the United States, sodium stannate is usually made from tin-plate scrap and other tin scrap. Consequently, it contains organic and other impurities.

A sample of British stannate was procured and with it the

A sample of British stannate was procured and with it the recommended bath produced the desired plate composition.

High-purity stannate can now be obtained in this country from the Metal and Thermit Corporation, Rahway, New Jersey.

Research also revealed that the bath should be held at operating temperature several days before use. Apparently some of the chemical changes are slow in taking place.

Full directions for operating this bath are given in Appendix I.

Manganese-Tin Alloy Coatings

Experiments on the Codeposition of Manganese and Tin

The investigation of this alloy grew out of a conference with Air Force representatives when the decision was reached to abandon the manganese-silver alloy in its favor. The manganese-tin constitution

diagram discloses that tin is soluble in manganese to the extent of 8% at room temperature. With higher percentages, intermetallic and possibly brittle compounds are formed. Compositions in the solid-solution range them became the goal for alloy plates.

Preliminary experiments for the electrodeposition of manganesetin alloys were reported in the Final Report dated June 28, 1949. The investigation has been continued with studies of the pyrophosphate solution and the thiocyanate solution. Neither of these solutions has produced a deposit of the desired composition.

The pyrophosphate-type solution produced the better appearing deposits, so it was used for the quantitative trials. By increasing the current density from 43 to 144 amps./sq.ft., the manganese content rote from 6.3% to 36%. A further increase in current density to 216 amps./sq.ft. raised the manganese content to 43%. It appeared that further increases in current density would result in smaller and smaller increases in manganese content. Thus, a 92% manganese deposit or higher from these solutions appears unattainable.

Lowering the tin content of the solution by 60% had very little effect on the plate composition.

Attempts to improve the pyrophosphate solution resulted in better appearing deposits, but the tin contents were still high. Experiments with a straight sulfate-type solution resulted in deposits having a tin content below 1%. Addition of a tartrate to the sulfate solution raised the tin content to the range 35-70%. The lower tin content was obtained

at high current densities. By raising the $MinSO_{l_1}\circ H_2O$ concentration from l_1O g./1. to 200 g./1., the tin content of the deposits was finally lowered to about 12%.

with both tertrate and exalate present, the hnSO, NZO concentration could be lowered to 40 g./l. to produce deposits with a tin content in the range desired. When the exalate was used in the absence of tartrate, poor deposits of uncertain composition resulted. Furthermore, the tin precipitated at a pH of 5 with only the exalate present. When both tartrate and exalate were present, no precipitation took place up to pH 8, at which point the bath seemed to function best. Current efficiencies are of the order of 15%.

Details of the experimental manganese-tin plating are given in Tables 21 and 22, Appendix I.

Static-Potential Tests

Table 6 gives the results of the static electrode potential tests on electrodeposited manganese—tin alloys in 3% sodium chloride solution. The data show two discrepancies in this series. The alloy containing 17% tin has a more noble potential than the 40% tin alloy. The "72%" tin alloy has a potential value which is less noble than the one containing "65%" tin. One apparent explanation is that the analyses were in error. The analyses were made on separate specimens plated under the same conditions, so it is also possible that lack of reproducibility in plating is the cause.

POTENTIAL-TIME DATA FOR ELECTRODEPOSITED MANNANESE-TIN ALLOYS IN THREE PER CENT SODIUM CHLORIDE SOLUTION AT 90°F. SATURATED-CALOMET SCALE, VALUES IN VOLTS.* TABLE 6.

Specimen					Volte of Ed			
Mubber	%Sp*	l Min.	30 Mins.	60 Mins.	90 Mins.	90 Mins. 120 Mins.	300 Mins.	330 Mine.
5022-29A	0.0	1.390	1,285	1.307	1.295	1.281	1,238	1.235
5022-33B	7. •0	ı	1.325	1.309	1.293	1,286	1.301	1.207
2052-48 B	11	1.197	1.203	1.172	1.157	1,133	1.163	27.1
5022-54D	07	1.191	1.312	1.246	1,200	1.175	021.1	7 · · ·
5022-40B	\$	0.768	0.730	0.879	0.913	0.917	2 6	ı
5022-41A	65		099*0	0.635	0.620	609-0	0 707	i :
5022-40A	72	0.780	0.937	0.9%1	076.0	0.939	0.928	• 1

* All values are negative.

One of the discrepancies in potential relationships was reflected in the degree of corrosion observed visually on the specimens. The "17%" tin alloy showed no brown corrosion products, while the "40%" tin alloy did. The specimens containing 59%, 65%, and 72% tin showed no brown corrosion products. Therefore, it is known that there are manganese—tin alloys having greater corresion resistance than has pure manganese at least in 3% sodium chloride solution, and which can be expected to give sacrificial protection to steel. What is not known is the exact composition for these alloys.

Experiments on the Preparation of Manganese-Tin Alloy Coatings by Diffusion

Subsequent experiments with the manganese-tin-plating bath showed the reproducibility to be poor. As with the zinc-silver work, time was an important factor, so rather than trace the cause of poor reproducibility, alloy coatings were prepared by diffusion.

In the work with electrodeposited alloys, those with a fairly high (about 40%) tin content showed prospects of having good corrosion resistance and of providing sacrificial protection.

The diffusion coatings which were prepared contained about 40% tim. Manganese was first plated on electropolished S.A.E. 4130 steel. Previous experience had demonstrated that electropolishing was necessary. Apparently, there was something on the surface of the steel which interfered with manganese deposition and which was removed by electropolishing. This may not be true for other lots of the same alloy. The tim was

plated directly on the manganese. The manganese-plated panel must be immersed in the tin-plating solution with the current on. Also, at the instant of immersion and for about five seconds thereafter, the current density must be above that normally used in tin plating. If those precautions were not taken, the tin did not completely cover the manganese, and where it did cover it blistered. Details of the manganese-tin duplex plating experiments are given in Appendix I.

No X-ray data were at first available for manganese-tin alloys.

Nevertheless, determination of the extent of diffusio. was possible.

Standard patterns for pure tin and for pure alpha manganese are known.

No evidence of free tin or free manganese could be found, so the conclusion was drawn that complete diffusion had taken place. Data for this test are contained in Table 7 and Figure 8.

Under the impression that interdiffusion of the manganese and tin was complete, several panels were exposed in the "wet-dry" cabinet.

The manganese-tin coatings showed better inherent resistance to attack than the pure manganese coatings. The characteristic brown corrosion products did not appear so rapidly on the alloy coating as on the pure manganese specimens. One specimen (4557-86C) had only 50 per cent of its surface covered with the manganese-type corrosion products after forty cycles in the "wet-dry" cabinet. The pure manganese coatings were covered with the brown oxides after only two cycles. The other three alloy coatings, while not so resistant as 4557-86C, did show improved surface resistance. As for providing sacrificial protection, however, the pure manganese was the better. After 134 cycles, the stee?

TABLE 7. DESCRIPTION OF MANCAHESE-TIN DIFFUSION COATINGS AND RESULTS OF I-RAY DIFFRACTION EXAMINATION

Specimen Number	Composition (Weight %)	Conditions For Diffusion	Order of Deposition	Renarks	Phases lient/fied Ey K-Ray Ciffraction*
4557-17B	60 Ln – 40 Sn	3 Hrs., 400°F.	in First	X-ray data for in-Sn alloys were not available at this time.	No free Mr, no free Sn
4557-37A	us 07 - un 09	3 Hrs., 400 F.	Mn Firet	İ	S-Sn + F-WaSn2
				One month after heat treatment.	S-Sn
				0.1 mil abraded of:	S-Sn + VF-kin
				Additional 0.1 mil abraded off.	S-Sn + S-Vn
5327-16A	5c Mn - 50 Sn	11 Hrs., 400°F.	Mn First		S-MnSn2 + extra line
		;		Abraded lightly.	F-wnSn2 + F-Wn
				7 days after neut treating un- abraded surface.	VF-MnSh2 + S-Sn
		e wilder van delde ve		Reheated, 5 hrs., 4.40 F.	S-Sn
				Powder removed, underlying surface examined.	u 9+0
5327 - 24.B	50 Pm - 50 Sn	S Hrs., 400°F.	An first, but 6 alternate layers alto-gether.	•	S-linsing
				5 days after heat treating.	VF-MnSn2 + S-Sn
· //^				Reheated, 5 hrs., 400 F.	VFMnSn2 + kS-Sn
				Forder removed, underlying sur-	F-4tnSn2 + 4-Sn

* The letters S, MS, L, F, and WF refer to the relative intensities (strong, nedium strong, medium, faint, and very faint) of that phase's diffraction pattern.

underneath pure manganese coating had not rusted. This was not the case with the alloy coatings. Three of them showed iron rust, which covered 5 per cent, 15 per cent, and 50 per cent of the surface, respectively. (See Table 2h. Appendix II.)

A better interpretation of these results can be made in the light of X-ray diffraction measurements, and so this discussion will be deferred until later in this report, where the X-ray results will be discussed. Following this, it was planned to prepare a series of manganese-tin alloys of different compositions. Calculations were made for alloys containing 10 per cent, 25 per cent, 50 per cent, 75 per cent, and 90 per cent tin. They were to be used for the measurement of potentials, which would define the composition limits within which sacrificial protection would be expected.

Shortly after this work was started, I-ray data were found which gave the identifying characteristics for manganese-tin compounds*. With the new information, a diffraction pattern was made from Specimen 1557-87A. (Table 7 gives the results for this and other manganese-tin specimens. Figure 10, Appendix II, shows the type of photograms obtained from the I-ray measurements.) The conditions for the preparation of Specimen 1557-87A were the same as for the panels exposed in the "wet-dry" cabinet. The diffraction pattern showed strong tin and faint 1mSn2 (Standard tin and Type A photograms, Figure 10). Some time following this diffraction measurement, the specimen was observed to have developed a gray powder

^{*}Hans Nowotny and K. Schubert, Metallforschung, 1, 17 (1946).

on its surface. This powder had not been there originally. The diffraction pattern obtained from this powdery surface showed only tin to be present. Successive abrasions showed the free-manganese pattern to be increasing in intensity (standard alpha-manganese photogram, Figure 10). Apparently, diffusion had not been complete. Also, with forty weight per cent tin, one would expect a compound such as Mn₃Sn, rather than MnSn₂. At this point, the preparation of the composition series of manganese-tin coatings was deferred until further tests were made in determining the conditions for diffusion.

Heat treating at the same temperature for a longer period (see Specimen 5327-18A, Table 7) resulted in a stronger MnSn₂ pattern.

X-raying after abrasion again demonstrated that the linSn₂ was only on the surface. Seven days following heat treatment, the powder had reappeared. After additional heat treatment, only tin was found. Several days later, the powder appeared once more. The surface underlying the powder was X-rayed and only tin was found.

These experiments were repeated, using, instead of a duplex plate, a coating with a total of six alternating layers, three each of manganese and tin. The total thickness was the same as with the duplex plate (0.3 mil). This was Specimen 5327-24B. Essentially the same results were obtained as previously.

The data from all these experiments show that the MnSn2 is concentrated in the outer layers. One explanation is that the manganese migrates along the surfaces of the tin pores and finds its way to the

surface. This phenomenen of surface migration has been observed with several other metal pairs. No reference to its occurrence in the case of manganese and tin has been found. The thin coatings of tin used in this work are undoubtedly porous.

The only thought on the formation of the powder is that linSn₂ is unstable and docomposes. Although manganese was not found when the powdered surface was X-rayed, it may have been present. Manganese does not give so strong a diffraction pattern as tin and could have been overshadowed.

The "wet-dry" tests can now be examined in a slightly different light. The so-called "manganese-tin diffusion coatings", as prepared thus far, appear to be triplex coatings, with a thin outer layer of manganese, an intermediate layer of tin, and an inner layer of manganese. Decomposition of the MnSn₂ layer would leave a duplex coating of tin and manganese. There is sufficient difference in potential between these two metals to cause rapid deterioration of the manganese, hence the rusting observed in three of the four "manganese-tin" coatings.

A few experiments were conducted where a manganese-coated steel panel was immersed in a molten stannous chloride bath. The manganese displaces tin in the solution and molten tin forms on the surface. The heat should cause the tin to diffuse into the manganese. A second inertsalt bath would be necessary after the requisite amount of tin is deposited. Diffusion could continue without additional deposition of tin.

Experiments on the preparation of manganese-tin diffusion coatings by electrodepositing tin on manganese in a fused-salt bath were discontinued because this method has too many practical disadvantages. The manganese and the tin tend to segregate, and only small amounts of Manganese detected.

In the previous work on manganese—tin, the heat treating was done below the melting point of tin. Heating a duplex manganese—tin plate above the melting point of tin did not increase the alloying; in fact, less alloying seemed to take place.

Examination of two of the codeposited specimens which were prepared some time ago disclosed an unidentifiable phase. This phase did not correspond to any of the phases reported in the literature.

Free tin was also found, but no free manganese was evident.

Manganese-Zinc Alloy Coatings

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Experiments on Manganese-Zinc Codeposition

Attempts to codeposit manganese and zinc began with a manganous sulfate bath to which was added varying amounts of zinc sulfate. It was found that the addition of one gram of 2nSO4.7H2O per liter of solution resulted in a bright deposit. Analysis of this deposit showed it to contain 90-95 per cent manganese. X-ray diffraction revealed an amorphous structure.

A rapid corrosion test was made on the bright deposits by placing several drops of distilled water on the surface. Within less than an hour the characteristic brown manganese corrosion products were visible, so that the inherent corrosion resistance of this coating appeared to be no better than that of pure manganese.

when two or three grams of zinc sulfate were added to the bath, a black deposit was formed. Changes in the plating variables did not result in a satisfactory plate when the zinc sulfate was higher than one gram per liter. The deposits were not improved by addition agents such as thiosulfate, gum arabic, licorice, and boric acid.

Experiments with Manganese-Zinc Diffusion Coatings

For the most part, the procedure in the preparation of diffused binary—alloy coatings has been to deposit the higher melting metal first. The manganese—zinc system was first attacked in this way.

The initial problem, of course, centered on obtaining adherent zinc deposits over the manganese.

Poor results were obtained with the special acid-type zinc solution used in the zinc-silver work. The zinc deposit was severly blistered. After several strike solutions failed to deposit adherent coatings, a dilute zinc cyanide strike solution was prepared and, by its use, better results were obtained.

Specimens with 0.3-mil-thick coatings containing 25 per cent, 50 per cent, and 75 per cent manganese were prepared and heat treated at 600°F. in air, for varying periods of time. Visual examination showed that, after four hours, the surface had darkened somewhat in color. In general, very little surface oxidation occurred during heat treating. When the manganese was plated last, the surface oxidized heavily.

Table 8 gives the heat-treating data and the phases found by X-ray diffraction. Reference to Figure 2 and Table 8 shows that

TABLE 8. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF MANGANESE-ZIMO DIFFUSION COATINGS. MANGANESE PLATED FIRST, EXCEPT AS NOTED.

Specimen Number	Composition ¹ (Feight %)	Diffusion Treatment	Phases Identified ²
5406-2 6 A	50Mm - 502m	8 Hra., 600°F., Air	S-engilon * F-beta Mn * VF-MnO
-340 ³	Ditto	23 Hrs., 600 F., Air	S-epsilon + MF-beta Mn + VF-MnC
-26F	π	4 Hrs., 600°F., Air	S-epsilon + VF-beta Mn + VF-Mr()
-34D	n	7-1/2Hrs., 600°F., Air	S-epsilon + F-beta Mn
~38A	75Mn - 252n	15 Hra., 600°F., Air	S-epsilon * MF-beta Ma
-38x	251m - 752n	15 Hrs., 600°F., Air	S-epsilon + F-beta Mn + VF-MnO
-74 0	75Mn - 25Zn	7 Hrs., 600°F., Air Cooled to 140°F. in Furnace in 16 Hours.	M-epsilon + F-beta Mn
-68F	50Mn - 50Zn	Ditto	S-epsilon + VF-beta Mn
-68 D	50Mn - 50Zn	н	S-epsilon + VF-beta Mn
-72D	25Mn - 75Zn	, vy H	S-alpha + ? Mm

1. Nominal.

3. Zinc plated first.

^{2.} The letters S, MS, M, F, and VF (strong, medium strong, medium, faint, and very faint) refer to the relative intensities of the phases' diffraction pattern. A question mark denotes that the identification of the phase was doubtful.

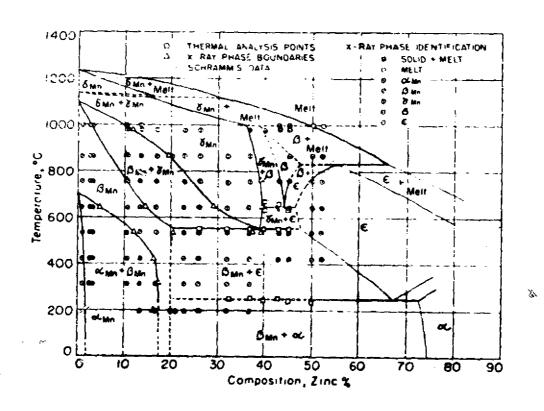


Figure 2. Manganese-Zinc Phase Diagram*.

^{*} E. V. Potter and R. W. Huber, Trans. A.S.M., 41 1001, (1949).

diffusion took place essentially in accordance with the phase diagram.

The most recent manganese-zinc phase diagram is reproduced in this report because it may not be readily available. The phases present (in the case of the 50-50 alloy) were those stable at about 572°F. (300°C.). The presence of these phases was thought to be due to air quenching when the specimens were removed from the 600°F. furnace. Another group of duplex manganese-zinc-coated specimens was heat treated in the same way but was furnace cooled at a slow rate. The data in Table 8 show that the slow cooling made no change in the results, except in the case of the 25 per cent manganese alloy.

Several specimens were prepared where the zinc was d posited first. These specimens oxidized heavily during the heat treating.

Table 17, Appendix I, gives some typical plating experiments in the preparation of manganese-zinc duplex coatings.

Static-Potential Measurements on Diffused Manganese-Zinc Coatings

Table 9 gives the results of static-potential measurements for three compositions of manganese-zinc coatings. The measurements were made in 3 per cent sodium chloride solution at 90°F.

These data show that sacrificial protection of steel can be obtained from these compositions. This is expected, since each of the elements is anodic to steel. The values at 360 minutes are in proportion to the manganese content. At the finish of the test, the beakers containing the sodium chloride solution were observed. A small amount of brown precipitate lay at the bottom of the beaker in which the

TABLE 9. STATIC-POTENTIAL MEASUREMENTS OF DIFFUSED MANGANESE-ZINC COATINGS IN 37 Nacl SOLUTION, AT 90°F. SATURATED-CALOMEL SCALE. VALUES IN VOLTS. POTENTIAL VALUES FOR MANGANESE, ZINC, AND THOM ARE INCLUDED FOR COMPARISON,

Specimen	Manganese			l at Elaps		
Number	(Weight %)	<u> 1 Min.</u>	30 Min.	50 Mia.	240 Min.	360 liin.
3180 - 370	100	-1.390	-1.317	-1.316	-	-
5486 - 38B	75	-1.282	-1.038	-1.042	-1.075	-1.107
- 70A	50	-1.177	-1.053	-1.053	-1.040	-1.039
-38 J	25	-1.035	-1.030	-1.031	-1.024	-1.Q6
2875 - 50B (Pure zinc)	0	-1.048	-1.056	-1.061	•	•
2875 - 33B (SAE 4130 steel)	-	-0,619	-0.709	-0.707	-	-

75 per cont manganese panel was tested. An equal amount of white precipitate was found in the beaker which contained the 25 per cent manganese panel. A much smaller amount of precipitate was observed in the beaker which contained the 50 per cent manganese panel. It appears that the 75 per cent manganese alloy corrodes very much like pure manganese, while the 25 per cent manganese alloy corrodes more like zinc. The 50-50 alloy had the better corrosion resistance in 3% sodium chloride solution.

Exposure tests with manganese-zinc, diffusion-alloy-coated specimens show this combination to have promise. The 50-50 coating has greater resistance than zine, but it is not so good as cadmium in the "wet-dry" test. This coating gives sacrificial protection and has an apparent advantage over pure manganese or pure zinc in that the corrosion products are more adherent and compact. Scattered, light-gray specks were observed on the surfaces of some of the specimens. (See Table 25, Appendix II, for details.)

One of the difficulties with the visual examination of these manganese alloys is the uncertainty in determining the initial rust. The color of the corrosion products of the coating hides the presence of iron rust. A non-destructive test on the corrosion product is required. Examination under ultraviolet light has been tried, but without success. Because of this difficulty, the determination of the first rust in several cases was questionable. The presence of rust was ascertained after the specimens were removed from the cabinet.

The 75 per cent manganese alloy corroded very much like pure manganese, as did the coating where the zinc had been plated first.

A second group of manganese-zinc alloys were exposed in the "wet-dry" cabinet. This group included three compositions, 25 per cent, 50 per cent, and 75 per cent manganese. The results are detailed in Table 27, Appendix II.

with the exception of two panels with coatings containing 25 per cent manganese, all the panels have lasted longer than those coated with pure zinc. This indicates that for improved resistance the coatings should contain about 50 per cent manganese.

During this second test, two of the panels showed small rust spots after a few cycles, but the rusted areas disappeared as the test progressed. This phonomenon had not been observed before. A possible explanation is that the nonferrous corresion products covered up the iron rust, and that finally the iron rust became sufficiently voluminous so that it could be seen.

Manganese-Copper Alloy Coatings

No work was done on manganese-coppor alloy coatings. It was mutually agreed that such work should be deferred until the Navy outdoor exposure tests on such coatings were completed. The development and preparation of the coatings was carried out by Graham, Crowley, and Associates* for the Airborne Equipment Division of the Bureau of Aeronautics under Contract No. NOs(s)9930.

^{*407} South Dearborn Street, Chicago 5, Illinois. 475 York Road, Jankintown, Pannsylvania.

Manganese-Nickel Alloy Costings

Experiments on the Codeposition of Manganese and Nickel

Codeposits of manganese and nickel were obtained using a regular manganese bath with small additions of nickel sulfate. Quantitative analysis showed these deposits to contain only 13% manganese. The deposits were not cohorent.

Pyrophosphate solutions containing both manganese and nickel did not give alloy deposits. Manganese, alone, was deposited from the pyrophosphate solution.

The compositions of the solutions used and the plating conditions are given in Appendix I.

Experiments on the Properation of Manganese-Nickel Coatings by Diffusion

In preparing manganese-nickel duplex plates, the manganese was deposited on the steel from the manganous sulfate solution. Sound nickel deposits on manganese were not possible from a Watts-type solution. For the most part, the nickel deposited in a blistered form, and, where it was not blistered, the adherence was poor.

A nickel strike solution (originally developed for plating on nickel die castings) was not effective in producing good deposits, either. Thin nickel deposits have been obtained in this laboratory from a cyanide bath. This was tried on the manganese and, after some experimental work,

was found to be effective. Because the cyanide solution stops depositing nickel when a flash plate has been attained, it was necessary to follow it with a plate from a Watts-type solution. Some typical runs are given in Table 18. Appendix I. The tests recorded in this table are the culmination of many unsuccessful attempts to make a manganese-nickel duplex plate. The heat-treating data, together with the X-ray results, are given in Table 10. The 75-25 composition was chosen for these tests on the basis of previous tests with cast alloys. (See Final Report dated June 25, 1949.)

When hoat treating at 600°F. for 8 hours resulted in no detectable diffusion, the same specimens were reheated at 1000°F. for periods ranging from 1-1/2 hours to 21 hours. Table 22 shows that, with increasing time in the furnace, the nickel and manganese lines became weaker, until, at 21 hours, their identifications were questionable. At the same time, iron became stronger, and a new phase, tentatively called the X-phase, became apparent. This X-phase has not been identified as yet. More work on these diffusion alloys will be necessary to clarify this matter.

Experiments with Zinc-Chromium Diffusion Coatings

No report has been found in the literature that gives X-ray data for zinc-chromium alloys. Diffusion may be detected by X-ray diffraction in the absence of such data, if the X-ray pattern shows no free zinc or free chromium, but does show some unknown phase. Of course, this train of thought can lead to an erroneous conclusion, as in the case of manganese-tin.

TABLE 10. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF MANGANESE-NICKEL DIFFUSION COATINGS.
MANGANESE PLATED FIRST.

Specimen Number	Composition1 (Weight %)	Heat Treatment	Phases Identified ²
5486-620	75Mn - 25Ni	1 Hr., 600°F., Air	S-Ni · F-Mn
-62D	Ditto	2 Hrs., 600°F., Air	pitto
-62E	1)	4-1/2 Hrs., 600°F., Air	Ħ
-62F	19	6-1/2 Hrs., 600°F., Air	n
-62G	10	8 Hrs., 600°F., Air	u
		"Additional Heat	
5486-620	75Mn - 25N1	1-1/2 Hrs., 1000°F., Air	S-N1 + S-Hn + M-Fe + VVF-X3
-6 2D	Ditto	3 Hrs., 1000°F., Air	S-N1 + S-Mn + M-Fe + VF-X
-62E	N	4-1/2 Hrs., 1000°F., Air	S-N1 + S-Mn + M-Fe + F-X
-62F	Ħ	6-1/2 Hrs., 1000°F., Air	M-N1 + ?-Mm + S-Fe + MS-X
-62G	ti	21 Hrs., 1000°F., Air	?-Ni + ?-Nn + S-Fe + S-X

1. Nominal.

- 2. The letters S, MS, M, F, VF, and VVF refer to the relative intensities (strong, medium strong, medium, very faint, and very, very faint) of the phases diffraction patterns. A question mark denotes that the identification of the phase is doubtful.
- 3. X- phase has not been identified, but does not appear to be a Mn Ni alloy. Some of the diffraction lines of this phase correspond to some of those of MnO. However, not all of the lines can be accounted for by this compound.

During the first year of work on this project, three compositions of zinc-chromium alloys were prepared in cast form. They contained 0.48 per cent, 2.04 per cent, and 5.36 per cent chromium, respectively. X-ray patterns were made for each of these alloys. The patterns showed an unidentified phase (the Y phase) to be present in the 2.04% and 5.36% alloys, the latter having the larger amount. The chromium contents of these alloys are relatively low, but it was thought, at the time, that the patterns might serve as guides in the diffusion work.

Duplex plates were prepared in two ways, with the zinc first and with the chromium first. Standard chromium and zinc (cyanide) solutions were used where the zinc was plated first. A special zinc strike solution was used for plating on the chromium. The solutions and conditions are given in Appendix II.

The results of the diffusion treatment are given in Table 11.

Some diffusion took place, as shown by the small amounts of Y phase.

Diffusion probably did not proceed for.

Experiments with Cadmium-Chromium Diffusion Alloys

No X-ray data were found in the literature for cadmium-chromium alloys.

The cadmium was plated first, and no difficulty was encountered in depositing the chromium over it.

It was thought that the cadmium and chromium would interdiffuse at a relatively low temperature, but such was not the case. The results are given in Table 11.

TABLE 11. DESCRIPTION OF CAST AND DEFUSED ZENC-CHROMIUM ALLOYS AND DIFFUSED CADMIUM-CHROMIUM ALLOYS AND RESULTS OF X-RAY DIFFRACTION EXAMINATION

er of sition irst irst	Composition Order of (GetCht I) Deposition C.LUS Cr(b) —— 2.OUS Cr(b) —— 5.36% Cr(b) —— 1 LLS Cr Zn First Cd 32 - Cr 18 Cd First	Conditions for Remarks X-lay Diffraction ^(a)	Cast alloy.	S-Zn + MF-Y	2 Hours, LOC'F. Gr flaked off. M-ray data S-3r + VVF-Y 3 Hours, 50C'F. obtained from pleces. 2 Hours, 60C'F. 14 Hours, 70C'F. 15 My atmosphere	22 Hours, 600°F., Negligible discoloration of S-Zn + F-Cr + VF-Y Air surface. Appears more Lustrous.	5 Hours, 500°F.
	- ω		•	 *			

The letters S. MS. M. F. WF. and WVF refer to the relative intensities (strong, medium strong, medium, faint, very faint, and very, very faint) of that phase's diffraction pattern. <u> </u>

Specimens -634-1, B-1, and C-1 were cast in the early phases of this project. 3

⁽c) I phase has not been identified.

Experiments with Manganese-Cadmium Diffusion Coatings

Mo special strike was necessary for plating cadmium over manganese. Good cadmium deposits were obtained from a standard bright cyanide solution at current density of about 18 amperes per square foot. This is somewhat lower than the usual 30 amperes per square foot customarily used with this bath. The only diffusion tests were made on panels having a 50-50 coating. In all cases manganese was plated first. No diffusion was detected after heat treating at 500°F. for six hours. Table 19, Appendix I, shows the plating conditions for preparing the duplex plates. Table 12 gives the heat-treating data and the results of the examination by X-ray diffraction.

Preparation of Outdoor Panels

The coated panels for outdoor exposure have been almost completed.

The details of their preparation are given here and will be given again several years hence when the results of the outdoor exposure are reported.

First of all, the preparation of each type of panel required some preliminary experiments to determine the current-density conditions for good plate distribution. After this, the plating was fairly routine, except in the case of the manganese-coated panels. A calibration curve for the measurement of manganese plate thickness with the Magne-Gage was not available. The calibration was made by first testing the thickness magnetically, and then, using exactly the same spot, measuring the true thickness of a micro section with a microscope.

TABLE 12. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF MANGANESE-CADMIUM DIFFUSION COATINGS.
MANGANESE PLATED FIRST.

	·		······································
Specimen SNumber	Composition1 (Weight %)	Heat Treatment	Phases Identified ²
5486 - 92 E	50 Ma - 50Cd	1 Hr. 500°F., Air	S - CD + VVF CdO
- 92 F	Dytto	2 Hrs. n n.	S - Cđ
- 92 J	• • • • • • • • • • • • • • • • • • •	6 Hrs. " "	S - Cd

1. Nominal

2. The letters S and VVF (strong and very, very faint) refer to the relative intensities of the phases diffraction patterns.

To date, the zinc-tin, pure manganese, and manganese panels have been coated. As this is being written, the zinc and cadmium standards are in preparation.

The plating rack, described in Appendix I, worked very well in producing deposits of uniform thickness.

Miscellaneous Experiments

Exposure Tests in the "Wet-Dry" Cabinet

Manganese Coatings with Tin Overlay. Manganese coatings will provide cathodic protection to the underlying steel. However, the manganese will deteriorate rapidly. As a means of reducing this rapid corrosion, thin coatings of tin plate were applied over the manganese.

Two tin-coating thicknesses, 0.00003 inch and 0.00006 inch, were used. Neither was effective in reducing the corrosion in the "wet-dry" cabinet. After one cycle, the surface of the metal was covered with brown spots. Flash coatings of tin are inherently porous and break down very quickly. Once this happens, acceleration of corrosion can be expected because of the formation of tin-manganese couples.

Cadmium-Silver Alley Plate. These deposits, containing 8% silver, were exposed in the scratched and unscratched conditions. Both types showed rust after a single cycle. It is important to note that the corrosion progressed fairly slowly after the first appearance of rust. At the end of 100 cycles, the pure cadmium was in better condition than

the alloy. The latter exhibited rust spots and scattered white corrosion products, whereas the cadmium had fewer rust spots and no white corrosion products. The cadmium-silver plate appears slightly inferior to the pure cadmium plate. While steel panels plated with zinc were not exposed concurrently, it is judged, on the basis of previous tests, that the cadmium-silver is superior to the pure zinc.

weight-Loss Results on the Cadmium-Silver Castings. Reference to Table 13 shows that cadmium-silver has about the same resistance to corresion in the "wet-dry" test as has pure cadmium.

Zinc-Nickel ("Corronized") Costings. The results for the "corronized" coatings are given in Table 26. Appendix II.

Three coating compositions were exposed. In all cases, the "corronized" coatings rusted before the pure sinc coatings, which were exposed as standards. The pregress & corrosion, following the initial rusting, varied with the composition. The higher the nickel, the slower the advance of rusting. It appears, from the results of this test, that, under conditions of moisture condensation, such as are met with in the tropics, these zinc-nickel alloys would not afford protection for steel. Observations of scratched zinc-nickel-coated specimens revealed that only a low degree of sacrificial protection could be expected where condensed moisture prevailed.

Whereas the nickel-zinc corronized coating appears to have achieved success under other atmospheric conditions, the results in the "wet-dry" test do not show such a coating to be a prospect for better protection than pure zinc in the tropics.

DOUTHETER PER DAY FOR CAST CADMINA-DELIVER SPECIMENS AND CAST CADMINA-DILIVER SPECIMENS AND CAST CADMINE SERVI-MAD ASTER SU DAYLY MATTERINE THE TERM THE PER PROGRAMS TRAT.

	:				
% Ag	Specimen Number	Weight Loss	Specimen Number	Weight Loss	Average Weight Loss (mdd)
0.0	2875-50A	1.33	3180-19F	1.47	1.40
1.24	2875-60AI	1.30	2875-60A2	1.47	1.39
3.04	2875-60BI	1.22	2875-60B3	1.38	1.30
7.95	2875-6001	1.41	2875-6002	1,29	1.35

 $\mathcal{F}(\mathcal{C}(\mathcal{C})) = \max_{i \in \mathcal{C}} ||\mathcal{C}_i||_{\mathcal{C}_{\mathcal{C}}}$

Cadmium-Tin Coatings. Both diffused and codeposited cadmium-tin alloy coatings were tested.

The specimens were supplied by the Naval Air Experimental Station, Naval Air Material Center, Navy Yard, Philadelphia, Pennsylvania. The diffused specimens measured 1-1/2 inches by 5 inches, and the coating ranged from 0.35 mil to 0.43 mil in thickness, as compared with the 0.3-mil coatings prepared here. The cadmium-tin coatings which were co-deposited from a fluoborate solution were plated on 2-inch by 3-inch specimens and represented thicknesses from 0.05 mil to 0.3 mil. Taking these variations into consideration, the codeposited alloy is believed to be somewhat more resistant than the diffused coatings. Of the cadmium-tin coatings, only the codeposited 0.3-mil-thick (3393-66L) coating prevented rusting and did not show tarnishing. The only change was a slight darkening. (See Table 25, Appendix II, for details.)

A report* received from the Naval Air Experimental Station,
Naval Air Material Center, Navy Yard, Philadelphia, discloses that the
cadmium-tin-alloy coating deposited from a fluoborate solution is
superior to both diffused cadmium-tin coatings and cadmium-plated
coatings in the salt-spray and humidity tests. Atmospheric-exposure
tests indicated that the fluoborate-alloy coating and pure cadmium were
comparable in the protection afforded and both were superior to the
diffusion-alloy coating.

^{*}Report No. Akl NAM AE 411027, Part II, Tin-Cadmium Alloy Coatings - Report of Tests, Issued 12 May, 1950.

A recent publication* by B. E. Scott and R. D. Gray, Jr., of wright-Aeronautical Corporation, gives salt-spray results for the cadmiumtin fluoborate coating. They report no rusting after 30 months in the salt-spray cabinet for coatings O.b and O.5 mil in Unickness.

Static-potential measurements in 3,3 sodium chloride solution were made on the specimens from the Navy. This was done to determine whether the coatings could give sacrificial protection to the steel.

The values are given in Table 28, Appendix II.

Coatings Which Do Not Give Cathodic Protection. Recently, some thought has been given to the possibility of investigating coatings which do not give sacrificial protection to steel, but which are not much more noble than steel. The initial test of this idea was made using a codeposited iron-chromium alloy. The method for depositing this alloy has been developed at Battelle under the sponsorship of the Army Ordnance Department. This alloy contains 5 per cent iron and 95 per cent chromium, and is deposited from a tri-valent chromium bath. Unlike the chromium deposit from the usual chromic acid solution, this alloy plate is free of cracks. It was thought that the crack-free nature of the plate would provide greater protection of the underlying steel. Specimens coated with regular hard chromium were exposed simultaneously as controls.

Rust appeared on the iron-chromium and the chromium-coated panels after two cycles. Two of the iron-chromium specimens were removed after 24 cycles, and the remaining two, after 64 cycles. The

^{*}Iron Age, January 18, pp. 59-62, 1951.

amount of rust was about the same on all four panels. The progress of rusting, beyond a certain point, is slow. Detailed results are given in Table 26, Appendix II.

Since experiments were being made with the electrodeposition of zinc-lead alloys, some pure lead coatings were exposed for comparison.

After two cycles, the panels were covered with loose, white corrosion products. After four cycles, spots of rust showed.

The Effect of Lightly Nitrided Surfaces on the Corrosion of Zinc Plate. A short investigation was made on the effect of nitriding the steel surface prior to plating. Zinc plate was used for this study, because more information is available on the behavior of zinc plate than for any other coating in the "wet-dry" test.

The panels with nitrided surface required an average of thirty eyeles—for initial rusting. The unnitrided panels showed the first rust after only 20 cycles. The advance of rust following the initial rusting was very rapid in both cases. The nonnitrided panels had 50% of the surface rusted after an average of 76 cycles, and the nitrided panels showed 50% rust after an average of 78 cycles. It can be concluded that, even though the nitriding delays the initial attack, the subsequent spread of rusting is so rapid that the difference in initial rusting has little or no meaning.

During World War II, it was reported that nitriding the surface of Armed Forces' tableware prior to chromium plating resulted in a higher degree of corrosion resistance than offered by chromium-plated

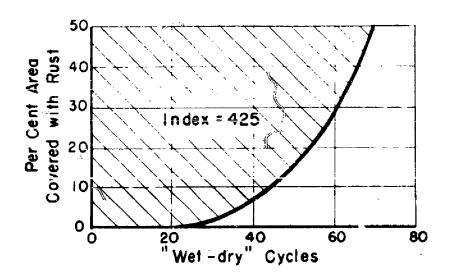
unnitrided steel. The type of plate which is deposited over the nitrided surface may also influence the results.

A Proposed Graphical Method for Improving the Interpretation
of "Wet-Dry" Tests. If the number of cycles to initial rust are used as
a sole criterion of corrosion resistance, it is entirely possible to
draw false conclusions. Such would be the case with manganese-zinc plate
on which one or two spots of rust appear after only two cycles. Assume
that the initial rusting on a zinc-coated-panel occurs after twenty
cycles. The zinc-coated panel may be 50 per cent corroded at seventy
cycles, whereas the manganese-zinc-coated stool, which rusted first, is
only five per cent corroded at seventy cycles. Thus, the progress of
further rusting after the initial rust is also an important factor.

It is proposed, therefore, to introduce a graphical integration method which includes the initial rusting and the progress of rusting thereafter.

Figure 3 illustrates this method. The limit for recording the extent of surface rusting has been arbitrarily chosen as 50 per cent.

A lower percentage can be taken if desired. The ordinate is chosen as the per cent area rusted, while the number of cycles are recorded along the abscissa. By taking the area of the shaded sections in Figure 3, a number is obtained (the "index") which gives the relative resistance of a coating. The upper curve shows how a zinc-coated panel might be represented. The lower drawing in Figure 3, which might symbolize the corrosion factor for manganese-zinc, shows earlier rusting but a very



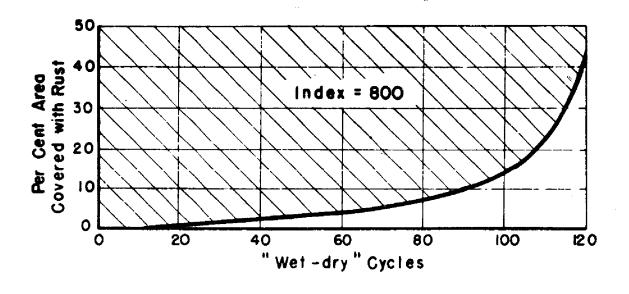


FIGURE 3. EXAMPLES OF A GRAPHICAL METHOD FOR INTER-PRETATION OF "WET-DRY"TESTS

slow advance of rust. The indexes show that the overall protective value of manganese-zinc is greater than that of zinc alone.

The method does not allow for differences in depth of penetration of the corrosion. During the three years that the "wet-dry" test has been in use, large differences have not been observed. If it is found in the future that there are significant variations in depth of penetration, then this factor can be added in:

The graphical method has been applied to some of the more recent tests. Table 27, Appendix II, gives the index values for plain zinc plate, zinc plate on a nitrided steel surface, and various compositions of manganese-zinc coating. The average index value for plain zinc is 439 and that for zinc on nitrided steel is 462. The index for the nitrided specimens is slightly larger, but not large enough to mean that an improvement has been brought about by nitriding the steel surface.

The results for manganese-zinc coatings show much larger deviations than do the aforementioned tests. Because of this, it may be necessary to apply statistical treatment to the results. This possibility is being studied. For the present, averages will be used. For the 25% manganese coating, the average index is 684, for the 50% manganese coating it is 878, and for the 75% manganese coating the value is 1187.

The main purpose in applying the graphical method to these tests at this time is to illustrate its use. It is believed that with refinements it can be developed into a useful tool.

Investigation of Corrosion Products. For some time it has been planned to study the corrosion products of the various coatings. One objective is to determine the influence of the alleying elements on the nature and extent of corrosion products. Knowing this, "designing" an alloy coating for maximum protection would be possible.

Preliminary studies of manganese-zinc corrosion products are given in Table 14. It is seen that zinc does influence the nature of the corrosion products. No attempt is made at the present time to correlate this information with other corrosion data. Further studies should be made before this is done.

EXPERIMENTAL WORK*

The apparatus and methods used for this work are described in detail in Appendix I. Appendix II is a collection of tabulated experimental data.

^{*}Laboratory Record Book No. 3393, pp. 57-100.
Laboratory Record Book No. 4557, pp. 4-100.
Laboratory Record Book No. 5022, pp. 1-67.
Laboratory Record Book No. 5327, pp. 1-58.
Laboratory Record Book No. 5351, pp. 1-81.
Laboratory Record Book No. 5486, pp. 1-100.
Laboratory Record Book No. 5561, pp. 1-30.
Laboratory Record Book No. 5617, pp. 1-23.

TABLE 14. X-RAY DIFFRACTION RESULTS ON MANGANESE-ZING CORROSION PROPUCTS

Specimen Number	Plate Composition (Feight %)	lin203•H20	lingO _{li}	Unidentified Phase
45 <i>5</i> 7-898	100%Mn	Strong	u -	с- •••
5486-38F	75Mn - 25Zn	Medium	Strong	Very Faint
- 76H	50km = 502m	••	Ditto	Medium
-76 D	25Mn - 75Zn	•	*	Medium

FUTURE WCRK

The future work comprises two phases under an extension of the contract:

- 1. Outdoor exposure of the coatings discussed earlier in this report.
- 2. Investigation of methods for electrodepositing binary manganese alloys. The manganese-zime, manganese-tin, manganese-copper, manganese-iron, manganese-molybdenum, manganese-nickel, and manganese-chromium systems will be studied, with the emphasis on the first two systems.

APPENDIX I

This Appendix contains descriptions of apparatus and methods used for the work described herein.

Preparation of Three Por Cent Sodium Chloride Solution for Static-Potential Measurements

The water used for the sodium chloride solution was the regular laboratory distilled water having a pH of 6.3. The salt was "Baker's Analysed" chemically pure sodium chloride. The solution was filtered and the concentration checked by accurate specific gravity measurement.

Static Electrode Potential Measurements

Apparatus

Figure 4 is a picture of the apparatus as set up for measuring static electrode potentials of four specimens concurrently. Also, pictured in the figure are the additional pieces of equipment used in the dynamic-potential measurements. No dynamic potentials were measured during the current phase of this project because of reasons given earlier in this report.

A Leeds and Northrup student-type potentiometer was used for making the static-potential measurements. Beckman No. 4970 saturated-calomel electrodes* were used as reference electrodes. Originally, a

^{*}Lianufactured by the National Technical Labs., Pasadena, California.



Apparatus for the Measurement of Static and Dynamic Electrole Potentials and Corrosion Currents. As Pictured, the Apparatus is Connected to Measure Static Electrole Potentials. Figure 4.

bridge was replaced early in this work with a salt-bridge junction tube described by G. A. Perley*. This bridge is nothing more than a Pyrex test tube with a soft glass rivet blown into a hole in the lower end. On cooling, the soft glass rivet centracts slightly more than the Pyrex, leaving a fine capillary crack. This crack is fine enough to keep the solutions on each side of the rivet from interdiffusing, but large enough to allow electrolytic conductivity. It has an advantage, too, in that it is more quickly set up than the former type.

The salt solutions were contained in 250-ml. beakers, which were immersed in a thermostatically controlled water bath (WB in Figure 4), which operated within 2 1°F. of the desired temperature.

The specimens were supported in bakelite clamps which rested on the edges of the boakers. A four-way, rotating, double-pole switch (S3 in Figure 4) was used so as to make possible the concurrent measurement of four cells.

The potentiometric circuit was calibrated twice by the Battelle Instrument Laboratory and was found to be accurate to 0.5 millivolt.

Method

Five milliliters of saturated potassium chloride solution were placed in the Perley-type bridge, the lower end of which was then immersed in the solium chloride solution. The Beckman calomel electrode

Trans. Electrochem. Soc., 92, 497 (1947).

was next immersed in the potassium chloride solution in the Perley bridge. The bridge was then adjusted so that the level of the sodium chloride solution is above that of the potassium chloride solution. In this way, any diffusion of the potassium chloride into the sodium chloride is minimized.

The clamped specimen was then immersed in the sodium chloride solution. After one minute, the initial potential measurement was made. This short elapse of time allows the specimen to "settle down" to a point where the potential is not changing very rapidly. Subsequent measurements were made at whatever time intervals desired.

The "Wet-Dry Program" Cabinet

A lead-lined, cork-insulated plywood box, measuring 3h inches x 25 inches x 25 inches, is the basis for the "wet-dry program" cabinet pictured in Figure 5. This box is equipped with a 1/2-inch-thick Lucite door (A) (letters in parenthesis refer to Figure 5), on which the specimens are supported by being clamped between Lucite washers in such a way that the test pieces do not make contact with the 18-8 stainless steel machine screws which pass through the washers. Twenty-four specimens can be exposed simultaneously. To prevent warping of the Lucite door, the edges were bound with angle iron.

The Lucite door is opened and closed in a predetermined cycle by a small motor (B), which, in turn, is actuated by a timing device (C) operating through relay (D). The motor (B) is a special type having two field coils, one of which "shades" the other, causing reversal.

P. L.

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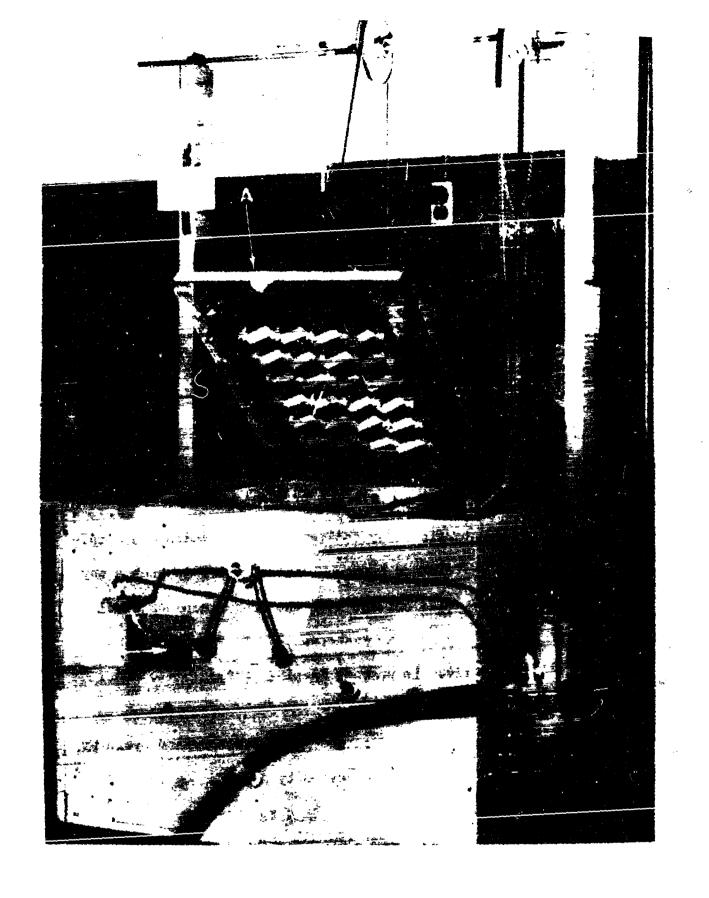


Figure 5. "Wet-Dry Program" Cabinat, Showing Boor Open and Corroling Specimens in Place.

To provide high humidity when the door is closed, water in a copper pan is warmed by an immersion heater. The pan measures 16 inches x 16 inches x 5 inches. The heater (electrical leads at F) is regulated by a thermostatic control (hidden by plate G), and operates only when the door is closed. A constant-level device (E) is connected to the copper pan and maintains the water at a 4-inch depth. The electric fan operates when the door is opened, cooling and drying the specimens. When the door is closed again, the fan stops, and in the humid atmosphere, moisture readily condenses on the chilled specimens. A schematic drawing of the electrical circuit is given in Figure 6.

Two minor changes in the electrical circuit have been made since Figures 5 and 6 were prepared. A new time control has been installed which allows greater latitude in cycling, and the original thermostatic control has been replaced by two controls connected in series and eperating through a relay. The additional control series as a series and eperated in the heater.



<u>Motor</u> - 110-volt A.C. Crise Electric Mig. Co., Columbus, Chio.
<u>Tire Control</u> - Two #303 controllers. Paragon Electric Co., Two
Rivers, Wisconsin. The switches of these timers are

connected in series. Both must be closed for current to pass through the circuit, but either one alone can break the circuit. Two controls were used because the

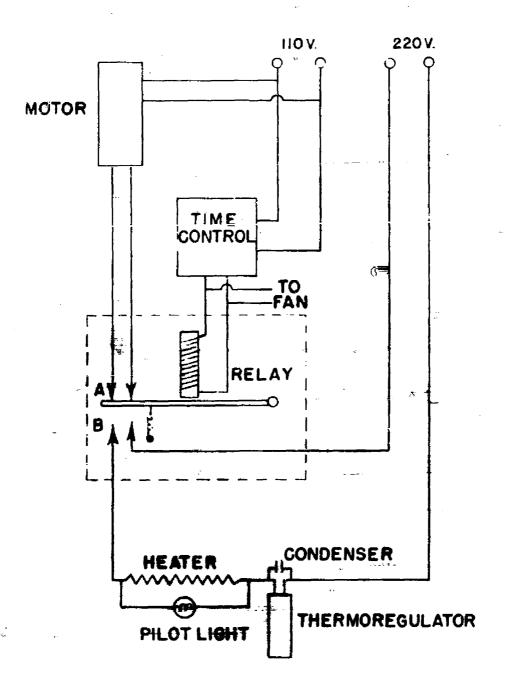


FIGURE 6. SCHEMATIC DIAGRAM OF ELECTRICAL CIRCUIT FOR "WET-DRY PROGRAM" CABINET.

- tabs on the circular time-setting plate could not be set for an interval as small as one hour.
- Heater Lo-Lag, 2000-watt, 230-volt copper-clad immersion heater.
- Relay Double-pole, double-throw relay. Struthers-Dunn, Inc.,

 Philadelphia, Pennsylvania. (Note: In Figure 6, the
 relay was not represented as being of the DPDT type for
 reasons of simplicity.).
- Thermoregulator Two, 110-volt, 10-amp. thermoswitches connected in series. Fenwall, Inc., Ashland, Massachusetts.

Removal of Corrosion Products for Weight-Loss Tests

The corrosion products were removed from the cadmium-silver castings and the pure cadmium castings by immersing the test pieces in 100 ml. of a 1 per cent solution of sodium cyanide at 70°F. for 20 minutes. After 10 minutes had elapsed, the surfaces were brushed lightly while the specimen was still immersed. A second 20-minute immersion in a fresh portion of solution, with brushing as above, completed the removal of the corrosion products. Blank tests showed the above treatment to remove only insignificant amounts of metal. Each specimen was examined at 20% magnification with a binocular microscope to be sure all nonmetallic material had been removed. The specimens were then reweighed and the weight-loss calcalations made.

Preparation of Experimental Diffusion Coatings

Apparatus

The plating apparatus used in preparing the duplex deposits preparatory to diffusion was in no way unusual. One- to three-liter quantities of plating solutions were used, and these were contained in Pyrex beakers. Heat was supplied to the solutions by thermostatically controlled glass-sheathed immersion heaters or by thermostatically controlled hot plates. The direct-current source was a 15-volt generator. The current was controlled by variable resistors, and Weston laboratory-model voltmeters and ammeters were used for voltage and current readings.

After the duplex plates had been prepared, they were heat treated in one of three ways to cause interdiffusion and alloy formation. At first, when it was believed that an inert atmosphere was required, the heat treating was done in a tube furnace. Later, the heat treating was done in regular heat-treating furnaces with an air atmosphere. A few specimens were diffused at 400°F. in a mineral oil bath. This temperature was too low, and was not raised because the oil had a flash point of 440°F.

Methods

Preliminary duplex plates were made on 1-inch x 1-inches x .015-inch SAE 1010 steel panels. Occasionally some of these were used in subsequent testing, but for the most part SAE 4130 panels measuring 1 inch x 4 inches x 0.063 inch were used for "wet-dry" and other testing.

The SAE 4130 test pieces were cut from strips measuring 4 inches x 18 inches, which had first been belt polished to a 240-grit finish.

The 1 x 4-inch test pieces were then numbered and stored in oil until "sed,

The plating methods are discussed individually below.

Zinc-Silver. The plating solutions, conditions, and finishing sequences for the zinc-silver duplex plating are given in this section.

Table 15 contains weight of coating data for several typical samples.

Anodic Phosphate Treatment for Promoting Adhesion of Silver to Steel

H₃PO₁ (85%) 500 ml.

H₂O 500 ml.

Temperature: 130°F.

Current Densityr 100 ASF

Time: 2 minutes

Cathodes: Stainless steel

First Silver Strike

AgCN 2.0 g./1.

KCN (free) 150 g./1.

Temperature: - 80°F.

Current Density: 5 ASF

TABLE 15. RESPECTIVE WEIGHTS OF SILVER AND ZINC IN DUPLEX COATINGS "HICH "ERE DIFFUSED AT 500°F. FOR ONE HOUR AND EXPOSED IN "ET-DRY CABINET. SURFACE AREA: SIX SQUARE INCHES.

	4557-75A	4557 -7 58	4557-75C	4557-75D
Weight of silver, g.	0.0729	0.0771	0.0742	0.0741
Meight of zinc, g.	0.2516	0.2539	0.2523	0.2521
Per cent silver	22.5	23.4	22.7	22.7

Zinc Plate*

 $Zn(CN)_2$

90 g./1.

NaCN

37.5 g./1.

NaOH

90 g./l.

Temperature:

120°F.

Current Density:

60 ASF

Anodes:

Zinc

Cyanide Dip

KCN

100 g./1.

Alkaline Gleaner (Anodic)

Anodex**

75 8/1.

Temperature:

200°F.

Current Density:

100 ASF

Finishing Sequence for Zine Silver Duplex Plating

- (1) Anodic, alkaline clean, 1 minute.
- (2) Hot-water rinse.
- (3) Anodie, phosphate treatment, 2 minutes.
- (4) Hot-water rinse.
- (5) Cyanide dip, 10-20 seconds.

^{*}This bath was used at first but was later replaced by a special acid solution developed for another sponsor. No permission has been granted to reveal its composition.

^{**} MacDermid, Inc., Waterbury 20, Conn.

- (6) First silver strike, 20 seconds.
- Silver plate, 5 minutes. (7)
- Distilled-water rinse. (8)
- (9) Cyanide dip.
- (10)Zinc plate, 5 minutes.
- (11) Cold-water rinse and dry.

The plating solutions, conditions, and finishing Manganese-Tin. sequences for the manganese-tin duplex plating are given in this section. Table 16 gives some typical examples of manganese-tin duplex plating.

Manganese-Plating Solution

linSOL°H2O

40 g./1.

(NH_L)250L

135 g./1.

Ne 203°7H20

0.5 g./1.

Tempera tura :

100°F.

Current Density:

45 ASF

Anodes:

Carbon rods in Alundum cups

Anolyte: (NH_{li})₂SO_{li}

135 g./1.

pH:

7.5

Tin-Plating Solution

K23:03:33:5

100 g./1.

NaOH

7.5 6./1.

TABLE 16. PREPARATION OF MANGANESS-TIN DUPLEE COATINGS

			Menganes	Wengenese Plating				Tin Plating	201/ 2 7	40		1	
Specimen Number	Tomp	Arre	C.D. (ASF)	Volte	(Fig.)		Initials	Finel	Intilate	Pinel.	Vol te	(404)	Remerke
"Azwo 1.	102	1.9	\$7	4	7.5	178	1.25	0.85	R	8	2.5		ë
7. est = 868	103 103	9.	57	•	7.5	•	•	•	•		•	•	Manginess deposit blistered at iigh-current-densi'r edgis.
ند. اعل	102	1.9	57	•	2.5	161	1.25	\$ 9. 0	8	۶	•	٢	fin plistered. Added 10 cl. eu. eulfite molution (0.1 g. Ne. 35.9-7H ₂ O/ml.) to mensione bets.
"Tunay"	٠ ۵	6.6	57	•	5.5		0.85	. 58. 0	&	٤	•	•	Tin blistered during plating Mangenese bath pH"7.6, Add 10 al. aulfite solution.
Pueny	*	1.9	45	•	7.5	371	0.85	0,85	8	Ş	•		Tip blistered.
7,22 - 860	ž.	1.9	57	•	5.6 2.5	173	3.0	0.80	72	19	•	۲	Excellent adherent deposit.
196 -	, A	1.9	3		7.5	174	2.5	0.90	\$	19	•	۲	Ditto
3 9 1	1 م	6.	57	•	7.5	174	2.7	ن _ة ي	20	19	•	۴.	This precimen analysed 42,99 tir.
- 86F	- -	1.9	57	3.8	7.5	175	2.0	0.8c	87	19	٠ ئ	,	Execilent adherent demest.
- 867	101	1.9	45	•	7.5	174	2.9	0.8c	٤	19	•	,	Ditto
- 86н	101	1.3	57	•	7.5	7.7	.	0.80	%	19	•	•	This specimen analysed 40.27 th. Added 10 ml. sulfite solution to manishes bath.
- 87A	302	1.9	45	3.8	7.5	174	**	0.80	<i>L</i> 9	19	2.5		Excilint adherent deposit.
- 873	102	1.9	45	•	7.5	174	3.0	ე 8 °0	2	19	•		Ditto
- 87C	& E	1.9	45	•		. 271	1.7	0.80	\$. <u>0</u>	•		This specimen analysed 21 25 time.

·, 9

. The current, was maintained at this value for five secretes. The manganese-costed panel entered the tin solution with the current on.

Temperature:

175°F.

Current Density:

20 ASF

Anodes:

Steel

Finishing Sequence for Manganese-Tin Duplex Plates ____

- (1) Electropolish*, 5 minutes.
- (2) Alkaline clean, anodic, 1 minute.
- (3) Hot-water rinse.
- (4) HCl dip (1 vol. 37% HCl, 3 vols. H2O), 3 seconds, 70°F.
- (5) Cold-water rinse.
- (6) Hanganese plate, 7-1/2 minutes.
- (7) Distilled-water rinse.
- (8) Tin plate. Enter solution with current on. (See Table 16 for time and current values.)
- (9) Rinse and dry.

Manganese-Zinc. The plating solutions, conditions, and finishing sequences for the manganese-zinc duplex plating are given in this section. Table 17 gives some typical examples of manganese-zinc duplex plating.

Manganese-Plating Solution

MnSOh • H50	40 g./1.
(NH _L) ₂ so _L	135 g./1.
Na2S03.7H2O	0.5 g./1.

^{*}Process of Battelle Development Corporation, Columbus 1, Chio.

TABLE 17. SOME EXAMPLES OF THE PREPARATION OF MANGANESE-ZINC DUPLEX COATINGS*

	Time (Ein.)	5.0	5.04	5.08	v 5.08 plated first)	2.57	7.69	5.08	5.08	7.69	2.57
Zinc Plate	C.L. (ESF)	3	-	=	u plated	\$	=	=	=	=	=
		30.1	1.04	1.04	1.04 (21nc	7.04	1.04	1.04	1.04	1.0	1.04
	Temp.	100	100	100	100		300	8 5	*	100	100
	Time (Sec.)	8	9	9	1	3	15	3	3	8	8
trike	C.D. (ASF)	87	17	77	strike	27	4	=		=	•
Zinc Strike	Amps.	2.0	1.70	1.70	<u>\$</u>	1.75	1.70	1.7	1.7	1.7	1.7
	Temp.	ଛ	8	80		&	&	æ	83	8	8
Вď	Time (Min.)	5.08	5.08	5.08	5.08	7.69	2.51	2.08	5.08	2.51	49°2
e Plating		57	2	=		5	=	2	=	•	=
Manganese	Ambas	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
	Temp.	%	100	100	100	100	100	102	•	100	102
	Specimen Number	5486 - 26A	- 26F	- 340	- 376	- 38A	- 38H	- 680	- 68F	- 72D	- 740

* Except as noted, the plating took place as given above from left to right.

Temperature:

100°F.

Current Density:

45 ASF

Anodes.

Carbon rods in Alundum cups

Anolyte: (NHL)2504

135 s./1.

ı Hq

7.5

Zinc Strike

 $2n (CN)_2$

5-7.5 g./1.

NaCN

5 6./1.

NaOH

5 5./1.

Temperature:

SO°F.

Current Density:

40 ASF

Anodes:

Stainless steel

Time:

1 minute

Note:

Immerse manganese-plated panel

with current on.

Zino-Plating Solution

 $2n(CN)_2$

90 g₃/1.

NaCN

.37.5 g./1.

NaOH

90 g./1.

Temperature:

120°F.

Current Density:

60 ASF

Anodes:

Pure Zinc (bagged)

Finishing Sequence for Manganese-Zinc Duplex Plates

- (1) Electropolish*, 5 minutes.
- (2) Alkaline clean, cathodic one minute, anodic 15 seconds.
- (3) Hot-water rinse.
- (4) $H_2SO_{j_1}$ dip (10% $H_2SO_{j_1}$), 10-15 secs., 80°F.
- (5) Hot-water rinse.
- (6) Hanganese plate.
- (7) Hot-water plus distilled water rinse.
- (8) Zinc strike.
- (9) Hot-water rinse plus distilled water rinse.
- (10) Zinc plate.
- (11) Rinse and dry.

ing sequences for the manganese-nickel duplex plating are given in this section.

Table 18 contains plating data for some typical examples.

Manganese-Plating Solution

MmSO₁₁·H₂O 40 g./1. (NH₁₁)₂SO₁₁ 135 g./1. Na₂SO₃·7H₂O 0.5 g./1.

^{*}Process of Battelle Development Corporation, Columbus 1, Chio.

TABLE 18. SOME EXAMFLES OF THE PREPARATION OF MANGANESE-NICKEL DUPLEX COATINGS*

Temp. C.D. Time Temp. C.D. C.D. (°F.) Amps. (C.D. °F.) Amps. (ASF) (Min.) (°F.) Amps. (ASF) (Min.) (°F.) Amps. (ASF) (Min.) (°F.) Amps. (ASF) (Min.) (°F.) Amps. (ASF) (Min.) 24, 45 8.17 80 1.0 24, 45 8.1	Specimen 3 9r		Manganose	se Plating	שע		Nickel Strike	Strike			Nickel Plate	Plate	
98 1.9 45 8.17 80 1.0 24 97 1.9 45 8.17 80 1.0 24 97 1.9 45 8.17 80 1.0 24		Temp.	Amps .		Time (Min.)	1 1	Amps.	C.D. (ASF)	Time (Min.)	Temp.	Amps.	C.E.	Time (Ein.)
97 1.9 45 8.17 80 1.0 24 97 1.9 45 8.17 80 1.0 24	2786 - 620	8	1.9	57	8.17	&	1.0	র	15	135	1.67	07	2°0
97 1.9 45 8.17 80 1.0 24	- 62D	8	1.9	45	8.17	8	1.0	ষ	15	136	1.67	07	2.0
	- 6213	8	1.9	57	8.17	8	1.0	র	15	138	1.67	07	2.0
	- 62F	8	1.9	45	8.17	80	1.0	র	15	138	1.67	07	2.0
- 626 97 1.9 45 8.17 80 1.0 24 15	- 620	8	1.9	45	8.17	8	1.0	*	15	136	1.67	9	2.0

* Plating took place as given above from left to right.

Temperature:

100°F.

Current Density:

45 ASF

Anodes:

Carbon rods in Alundum cups

Anolyte: (NH_L)2SOL

135 6./1.

pH:

7.5

Nickel Strike Solution for Plating on Manganese

Ni(CN)2

91.3 6./1.

KCN

103 6./1.

Na28407.10H20

20 g./l.

Temperature:

80°F.

Current Density:

24 ASF

Anodes:

Steel

Nickel-Plating Solution

NAS 0/1 • 7H2 0

300 g./1.

Ni Cl2 6H2O

50 g./1.

H3B03

35 6./1,

Horshaw XXX-D*

20 ml./1.

Note: This solution was purified by the usual methods.

^{*}Harshaw Chemical Company, Cleveland, Chio.

Temperature:

135°F.

Current Density:

40 AJF

enedos:

Cast mickel in cass

pH:

2.8

Finishing Sequence for Manganese-Nickel Duplex Plates

- (1) through (7) Same as for manganese-zinc.
- (8) Nickel strike.
- (9) Hot-water rinse plus distilled water rinse.
- == (10) Nickel plate.
 - (11) Rinse and dry.

Zinc-Chronium. The plating solutions, conditions, and finishing sequences for the zinc-chronium suplem plating are given in this
section.

Chromium-Plating Solution

cro₃ 250 g./1.

sol 2-5 6./1.

Tungarature: levis

Ourrent Density; 225 ASF

Anodes: Antimonial lead

Zi..c Strike

ZnO

2 (./1.

H₂SO_L (96.5)

10 ml./l.

Temperature:

70°F.

Current Density:

120 ASF

Time:

15 seconds

Anodes

Lead

Zinc-Plating Solution

Zn(CN)2

90 g./l.

MaCN

37.5 g./1.

NaOH

90 g./1.

Temperature:

120°F.

Current Density:

60 ASF

Anodes:

Zinc (bagged)

Finishing Sequence for Zinc Chronium Duplex Plating when Zinc was Plated First

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3N H₂SO_h, 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) 10 seconds'dip in 10% NaCN solution, 70°F.
- (6) Cold-water rinse.

- (7) Zinc plate.
- (8) Hot-water rinse.
- (9) Chromium plate.

Finishing Sequence for Zinc-Chromium Duplex Plating When Chromium was Plated First

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3 N H₂SO_h, 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) Chromium plate.
- (6) Hot-water rinse.
- (7) Zinc strike.
- (8) Cold-water rinse.
- (9) Zinc plate.

Cadmium-Chromium. The plating solutions, conditions, and finishing sequences for the cadmium-chromium duplex plating are given in this section.

Cadmium-Plating Solution

Gadolyte single salt* 120 g./l.

Temperature:

30°F.

Current Density:

25 ASF

Anodes:

Steel

^{*}The Udylite Corporation, Detroit 11, Michigan.

Chromium-Plating Solution

Cr03

250 g./l.

ՏՕև

2.5 g./1.

Temperature:

<u>1</u>20°F.

Current Density:

225 ASF

Anodes:

Antimonial lead.

Finishing Sequence for Cadmium-Chromium Duplex Plating

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3N H₂\$O_h, 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) Ten seconds dip in 10% NaCN solution, 70°F.
- (6) Cold-water rinse.
- (7) Cadmium plate.
- (8) Cold-water rinse.
- (9) Chromium plate.

Manganese-Cadmium. The plating solutions, conditions, and finishing sequence for the manganese-cadmium duplex plating are given in this section.

Table 19 contains data for the preparation of some typical specimens.

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	2		
		11	

}	Menganese Plati	Plating		O	Cadmium Plating	Plating	,	. "
Specimen Tomp.	Amns	C.D. (ASF)	Time (Fin.)	Tong.	Amps.	C.D. (ASF)	(Time	Remairks
2486 - 920 98	1.9	57	5.6	8	0.75	18	6.4	Satisfactory duplem plate,
- 92E 100	1.9	2	3.6	8	0.75	*	6.7	Ditto
- 92F 100	1.9	*	5.6	8	0.75		6.4	82
- 926 100	1.9	Ė	2.6	8	2.0	*	1.84	Cadmium plats blistered.
- 923 98	9.4	*	5.6	8	0.75	*	6.7	Satisfactory duplex plate.
- 92K 100	1.9	£	5.6	8	1.0	£	3.7	Cadmium plate blistered on one side.

Manganese-Plating Solution

linSO_h•H₂O 40 g./1.

(NH_L)₂ SO_L

135 g./1.

Na2S03.7H20

0.5 g./l.

Temperature:

100°F.

Current Density: 45 ASF

Anodes:

Carbon rods in Alundum cups

Anolytes (NH_{l1})₂ SO_{l1} 135 g./1.

pH:

7.5

Cadmium-Plating Solution

Cadolyte single salt* 120 g./l.

Temperature:

80°F.

Current Density:

30 .\SF

Anodes:

3tecl

Finishing Sequence for Manganese-Cadmium Duplex Plating

- (1) through (7) Same as for manganese-zinc.
- (8) Cadmium plate.
- (9) Rinse and dry.

The Udylite Corporation, Detroit 11, Michigan.

Zinc-Silver Codeposition

Small portions of solution, usually 100 ml., were used in the zinc-silver codeposition experiments. The usual apparatus, consisting of variable rheostat, ammeter, voltimeter, etc., was used. The solutions were contained in a beaker and were heated by immersion in a thermostatically controlled water bath.

Table 20 contains the details of experiments in the iodide solution. The details of the composition and operating conditions for the thiosulfate solution are given below.

Thiosulfate Solution and Conditions for Linc-Silver Electrodeposition

	$Na_2S_2O_3(anhyd.)$		200 g./l.
	AgNO3		3.6 g./l.
-	Na2SO3.7H2O		0.36 g./1.
	ZnCl2	6° - 6° - 40° - 7°	35 g./l.
	H ₂ SO ₄ (Sp. Gr. 1.85)		0.36 ml./l.

Solution used with agitation and with or without 2 g./l. gelatin.

Anode:	Carbon
Cathode:	Stainless steel
Current Density:	18 ASF
Temperature: "	70°F.

TABLE 20. ZINC-SILVER ALLOY PLATING EXPERIMENTS (TOWIDE SOLUTION)

4557 - 9A NaI 520 8./1. Cutric acid 608./1. Ag2 - 9B Ditto - 9C Ditto - 1 8./1. Napthalene 1, 5, - Disulfonic scid - 9D Distro - 10A - 10B - 10C - 10D - 10C - 10D - 10D - 10C - 10D 20 F1 8	**************************************	1			2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Repalte	
Ditto * 1 g./l. Napthalene 1, 5, - Dimulfonic soid Ditto	71 19 8		1.35	4	Carbon	Stainless steel	Powdery surface. Underlying deposit adheren fairly well and is compact.
Ditto * 1 g./l. Napthalene l, 5, - Disulfonic soid Ditto	ደ 8	8 0	0.97	10	Ditto	Ditto	Powdery deposit who off essiy.
Ditto	8	10	1.35	4	•	•	Same au 9A.
* * * * * * * * * * * * * * * * * * *		80	1.2	•	•	SAE 1010	Better than 94, 55, or 90. Deposit had a sliver mat polor. Less powdery.
* ************************************	*	80 80	7.1	€	•	Brass	Dark plate. Powdery surface.
	8 8	0.07	2.75	.	•	Stainless steel	Gray plate. Powdeny surface.
	&	35.0	1.95	12	•	Ditto	Dark gray plate./ Fowdery surface. 7.5% allver.
	8	10.0	1.25	*	•	•	Dark gray plate. Powdery surface.
	8	°°	1.23	£	•	•	Gray deposit. Powdery surface. 50.3% silver. (Note: This experiment differed from the three preceding, in that there was no addition agent and the temperature was lower. It is included as a fourth point for Figure 1.
4557 - 12A Ditto	8	20.0	1.55	01	•	•	Postery surface. Underlying surface is sound. About 0,25 mil thick.
- 128 Ditto + 1 g./l.	8	50° 0	1.52	30	•	•	Disto
Bets maphwhol-12C 12B thiowrea	8	20.0	1.55	0		•	Ditto, but outer layer darker and thickpr.
- 12D 12C * carbon disulfide	85	30.0	1.6/	01	•	•	Same its 12A and 12B.

TABLE 20. (Continued)

Reaul C.	Phits deposit, Mearler gassing. Positive test for silver, Negative test for zinc.	Hard nodular plate, part of which acraned oif welly. Dark gruy. Silvar and a use present. Some inprovement over higher temperatures.	Medium gray plate. Less pondery,		Agitated mildly. No improvement.		Medium agitation. No improvement over still solution.	Medium agitation. No improvement		•	Rabid agitation. No improvement	Q	Black powdery deposit.
Cathode	Stainless steel	Ditto	• ` : : 4	•	•		•	Brass	Stainless steel	Ditto	*	•	•
Anode	Carbon	Ditto	*			frents.	•	•	•	æ	•	•	•
Time (Fin.)	10	01	10	55	10	wing exper	10	۲	10	10	10	8	in .
Volte	•	1.75	1.3	1.7	1.75	in the following experiments.	1.53	1.53	1.53	1.53	1.53	1.35	4.5
Current Density (Amps./Sq.Ft.)	20.0	20.5	20.0	20.0	20.05	er, was used	٥. ٪	20.0	2C•0	20.0	o•0;	10.0	100.0
Temper- ature (°F.)	8	07	07	07	27	magnetic sti	8 2 8 2	86	%	85 82	85	85	80
Bath Composition	12D + 5 ml. HU	Same as 4557 - 9A	Ditto + beta naphthol	13B * reservinel	Disto	Agitation, supplied by a magnetic stire	Same as 4557 - 9A	Ditto	Ditto + beta machthol	14C * resorcinol	Ditto		Same as 4557 - 9A
Seet Number	4 FFT = 128	+ 13A	- 138	- 130	130		- 174	- 17B	- 140	- 17D	- 145	- 14F	- 20 4

TANDA XI, PRINCIPLES INDICAPESE-TER ELECTRODEPOSITION EXPERIMENTS

								ŧ						
Additions to Bath at End of Test	કું 🖽 ે	50 g. mrs02.H20		Ditto		id. It was evident at aps./sq.ft. through was present as a trace	4.5 g./l. SnSO4 added	7						
See all the second seco	Positive test for manganese, trace of tin-	Trace of tin, no manganese.	Positive test for mangenese, trace of tim.	Ditto	Trace of manganese, trace of tin.	The mangenese solution of this bath was made un in promortions recommended in U.S. Patent No. 2,398,614. It was evident at the start of the oreliainary tests that the tin was sludging out. Cathode C.L. was varied from 40 amps./eq.ft. through 144 amps./eq.ft. pH of bath held at 4.0. The deposited as a porous, nonadherent aludge. Mangenese was present as a trace in the thin layer under the tin.	Thin, black, nonadherent deposit Heavy indication of manganese, trace of tim-	Black, thin, adherent deposit. Trace of manganese and trace of tin.	Black, thin, adherent deposit. Positive indication of manraness, trace of tin.	Top portion of deposit mat color, bottom rough, black. Same analysis as above.	Thin black deposit. Trace of manganese, trace of tin.	Pough, black deposit. Positive indication of manganese, trace of tin.	Slack, porous, nonadherent top layer. Thin, dark, adherent deposit undernesh. Fost-tive indication of Mn. Tree of Sn.	Dick sponge tin leyer, nonadherent. Thin, black, wherent deposit below. Trace of manganese, trace of tim.
Cathode	Stainless steel	Fitto			•	in proporti was sludgi poelted as	Stainless steel	Ditto	•	•		*	•	
Anode	Lead-silver alley 99% Pb-1% Ag	3.12	•			s both was made un 'tests that the tin held at 4.0. The dintin	Lead-silver alloy (99% Pb-1% Ag	bitto		•	•		•	
Time (Min.)	7.5	30	10	10	8	n of thi liminary of bath	57	91	٠.	10	ž	R	۶	30
12	8.0		•	•	•	solutio the ore ft. pH	٠	9.7	9.7	9.7	1.	3.6	3.6	3.6
Current Density (Amps./Sq.Ft.)	07	07	27	77.	27	The mangenese solution of this have the start of the ureliminary test 14, amps./sq.ft. pH of bath hild in the thin layer under the tin.	150	150	77.	250	67	288	771	73
rent (82	78	82	\$ 0	08	P	87	82	84	78	78	78	78	8 3
Bath Composition		Sn-K-P.O. solution.	K.P.O. 300 g./1. SnS7, 58./1. Beta naphthol 1 g./1.	Hide glue 2 g./1. Adjust pH from 9.5 to 8.0 with H25%		76 8.7. 50, 75 8.7. 60 8.7. 4.5 8.7.	50, 76 8./1.	phtho]		-				
.		Ma20∪3	K4P207 SnS34 Betan	Hide g Adjust		MASO, H. (NH,) SK NH, CNS SnSO,	MA 50, 470 (NH) 250, NH, 500, NH, 500,	Betana Gelatin Cresol						
Rath Type and Mumber	64 Pyrophosphate 5022 - 54	89	9	60	5 2	Ammonium thiocyanate 5022 - 9A	5022 - 11A Ammonium thiosymmate 5022 - 10A	; .	9	9	š e	ß .	ဗ	=
Test	5022 -	•	•	•	1		5022 - 1	- 118	- 110	- 11b		- 11	- 116	#E

Manganese-Tin Codeposition

One liter portions of the solutions were used in the manganesetin codeposition experiments. Again, the usual type of apparatus was used.

Tables 21 and 22 give the experimental details for this work.

Manganese-Nickel Codeposition

The solutions and conditions used in the manganese-nickel codeposition experiments are given below.

Solutions and Conditions Used for Langanese-Nickel Codeposition Experiments

Ammonium Sulfate Type

Solution A.	lanS0 ₄ •H ₂ 0	40 g./1.
	(NH _L) ₂ 50 _L	132.5 g./1.
	Na2SO3.7H20	0.25 g./l.
	pH adjusted	to 7.5 with 1-1 HH,CH

			11.0	-	Analysis of	(4)	5033 702 tage	1) Intelligence	
	4	Mark Carlotter of the Control of the	intent	- 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	or and were or maked, beatment est op or or or and on or		anoder gestlelfA	anobes questionablag more usud, carredus Bere of gradulass site.	The self was to the self of th
			-						ig plant
··	•	· · · · · · · · · · · · · · · · · · ·	· · Mmor	רייבליץ.	المريع./١٠. الري المائفة - 197	Pothosp	چه ده هو ايم-دريم	standing sulfate of prothosphate solution - 10 sl./1.	wilker e
		:		9	1	•	•	15h. 15B, and 15C, derosits were adverent and om oth.	- grade
	, 1 =	25 771		12					SC MILL Maping Conference Contraction
	. •	'n	•	~	•	,	•		· Št.
	•	.		y: G	. 1		, • 1	POSSENTUNING CERTIFICATION OF SCHOOL OF THE POSSENT	o de la companya de l
		777				•		of cell depleting manyanese content of their.	
			9 400	, oe#- / c/s	-308./1., KE	P20-53	H20-312	in it enclose a second and a second of the part of the part of the second of the solution - it is in the second of the se	TON BUT I BE SOUN TO THE TO THE
, ,		Path comost	יושע 1 ווניני	3	•	-		and the second s	
•	á	Š	•	2/2-22	17-1/2 Balence	٤:		Deposite and a second of the contraction of the con	
# - ';	•	7	•	۲.	. •	7 E		د	
	•	عاد ا	٠,	-7 ;	. :	<u>,</u> •	•	17A - mat color deposit.	73
	c. 1	12.4	No ~	<u>.</u>	• •		3	٠	••
r 8			3 ⁄0	,			•	•	
		•	180	•	•	,	•	The court process	-
_	=	*	10	•	•	,	•	•	
t e		Rath commons	tion 1 Mm	76H. 7USI	0-60p./1., K	(P207°)	M20-312	Bath commestition a MnSD, 1420-409./1., K_P2O7-3M2O-312@./2., Na2SO3-50ml. (.OK5g./1. soln), 3-11ter volume buth.	Y
4				*					
# 484 11 V	6	\$	•	8	•		. 1	20 D1918	The reference to the second of
a au	æ	330	* ,	၃ န	. (, sc	The toleto	程 · 10 · 10 · 10 · 10 · 10 · 10 · 10 · 1
# W.K.	ĭ	5	ur i	3.		Trace.	. =	Sightly thicker deposit	**************************************
6 0), 1	•				Prattive		•	Good-sphearing deposit	A CONTRACTOR OF THE PARTY OF TH
ا تع دري ا		. •	. =	•	•	•	•	No antractable increase in an content.	
**************************************	-	Bath composi	ition :	150,472) *** (*******************************	22(7HM)	0,-135g	Bath composition : MmSGA. H20-40g./1., (WHA) 250,-135g./1., NmpSG3 (.005g./ml.)-50 ml./1.,	
			Ġ) I M				SAME TO TO SAME TO SAME THE PROPERTY OF THE PR	•
* 45 CHAACE	C	7.2	6.2			, %	• •	March thought good appropriately as a second	
-25B =			• 4	, K	Baranca -	<u>;</u> ,	•		. ,
■ 050-	•	•	;				;	A same of the Altter volume	
794		Bath compos	ition : #	H. Yusu	20-404-/1	(NEW) 25	30,-137	Bath composition a Massign Apo-40g./l., (MRA)290g.137 g./l., Napsug 18./h., /	e sy
		;	;	:	-	1	•	all deposits in this group good that color deposit.	

	ere	,		,	" 2				
Additions to Bath at End of Test	0.5 g. Ma2SO3 crystals	2	Bath filtered		13 g./l. SnSO4 added	·			
Results	Thick sponge tin layer, nonadherent. Thin, black, adherent decest below. Trace of manganese, trace of tin.	Smooth, thin, dark met deposit. Positive indication of manganese, trace of tim.	Rough, acherent deposit, Positive indi- cation of manganese, positive indication of tin.	faich black deposit, rough surface adherent. Trace of sanganese, positive indication of tin.	Ditto	Black, nonmetallic arrearing, scherent deposit. Positive indication of manganese, trace of tin.	Continuous, dark mat, smroth, good adher- ence, 6.3% km.	Dark, alightly rough, good adherence. 36% ma.	Black color, rough surface, good adherence. 43% Mm.
Cethode	Stainless	Ditto	•		•	•			•
Anode	Lead-silver alloy 99% Pb-1% Ag	Ditto			•	5		•	
rime (Fine)	15	77	6	. 15	15	8	•	9	•
' E	3.6	0.4	0.7	0.7	c. ;	0.7	8 °0	ت. ص	ပ ့်
Current Density (Amps./59.71.)	57.	25	288	288 (9 volts)	216 (7 volts)	007	67	771	216
fem.	82	87	82	28	789	82	16	86	78
Beth Composition	7		s Ž				MnSOg.E20 R4P2O7.3H2O.225 ml. of 800 g./l. moln.	Mag80g soin. (.005 g./ml.) 50 ml. Add 50 ml./l. of the following soin.	N. P. Dr. 3H20 300 g./l. Sh.St. 55 g./l. Beta naphthol 1 g./l. Gelatin 2 g./l.
Bath Type and Rumber	5022 - 111 Ammontum thiosymate 5022 - 10A	- 11J (Continued)	<u></u>	;	=	_	5022 - 134 Pyrophomphate 5022 - 124		
Test	5022 - 11	п.	- 11K	. 111	MII -	. YLL -	5022 - 134	- 138	- 130

Additions to Bath at End of Test						25 ml. modified ammonium stannous oxalate solution.	Bath became cloudy. 25 g. tartaric acid added, pH adjusted to 7.5. Cloudinese did not respect.		5.0 ml. modified salution added to beth.	
ล : [กล ค.:	Smooth, adherent, metallic mat grey plate. 1/2-inch diameter, steinlers steel cethode used. Smooth, adherent met gray deroait.	SnSO ₂ -1.0g./l., tartaric acid-25g./l., hide glue (hydrolyzed solution)-C.lg./l., (RH ₄) ₂ SO ₄ -200g./l., MaSO ₄ -R ₂ O-100g/l., Ma ₂ SO ₃ -0.5g./l. 3-liter rolume.	Good-appearing mat denosit. Good deposit, EnQ2 darkened beth.	Good-appearing mat denosit. Lower tin content result of 5 hours dummying. Smooth, adherent mat gray deposit.	2,-135g./1., We2303-0.16g./1. dxalate solution" -3,3ml./1.	Very good deposit, emooth, echer-nt, mat color-	Analysis not completed, tin too high.	<pre>mmSO2.HgO-4Cg-/l., (WH2/)2502=135g-/l., NspSO3=C.25g./l. Tarferic acid -8g./l., modified stannous ammonium oxalate solution -3.3 ml./l. 3 liter volume bath.</pre>	Sample lost in furnace during ignition. Smooth ast color deposit,	Smooth, 34 erent, wat deposit.
Cell Voltage	5:5	14-25g./ 20-100g/	9.6		,-135g./ dxalate	5.5	8.0	(196 star	8.2 6.8	C.#
s of	17.0	tario ac	40.76 40.82	11.3 13.4 12.8 15.2	(NH _L) ₂ 80 tennous	Mone •	Honvy	(MHg,)280, 1., mod1	1 6.9	7.9
Analysis of Deposit	Balence	0g./1., tai	Balance	Balance	Maso, 49,0-40g./l., (NH,)280, Modified amonium stannous	Heavy	F	<pre>im.SO2.8204.826./l., (MR2/2802-135g./l., Mapl Tarteric acid -8g./l., modified stannous as solution -3.3 ml./l. 3 liter volume bath.</pre>	Balande	Balance
11 mg	15	n50,4-1.	15	* * * *	280, 'H2	15	15	1504.HZ irteric olution	15	& •
	0		7.5	****		7.5	7.6		,	0•ສ
Current Density (Amre,/Sq. Pt.)	0***	Bath composition:	270	9	Bath composition:	120	132	Bath composition:	216 120 •	120
Tomp.	92 88 88		120 30	250 2118 118		115	28 8%		88.	120
No th	T	53A	¥	• • • • •	37 8	57.4	• •	7 09	₹	
Test	5022-494 504 508 508 518		5022-54A 548 548 540	27.48.8 34.48.8		5022-574 -584	594 598		\$022 604 \$03 \$03 \$00	7.9

* Preparation of the modified stannous amonium oxalate solution: 25g. tartaric acid dissolved in 1° ml. distilled water and added to 2°C ml. stannous amonium oxalate aclution. If precipitate settles out, dissolve by heating the solution to 100°F. Adjust pH to 7.5.

								ē				
Additions to Bath at End of Jest		SnSO ₄ -1.(<i>p./</i>).					nous exalste solution - 20ml.	40 ml. Amon. stamone oxalete 100 ml. Amon. stamone oxalete Solution boiled 1-1/2 hours with sponge tin.	- 25 g./l., hytrolyzed hide glue solution -		Ž.	1. Pris. 13, 1508./1. 2. (Ni. 125
Republe	Bath composition : MnSCv-M20-40F./1., (WM1)2SCv-137 g./1., 'eo2Sq-7.25g./1., 3-11trr volume bath.	Cathode aritated. Cook mat color deposit. S.A.E. 1010 cathode. Static risting conditions. Agitation of bath, static cathode.	a a series of cathods.	Ferun of Test 5022-32A.	$(NH_{\star})_2SO_{\star}=75g_{\star}/1$, $NH_{\star}/VS=\{0g_{\star}/1$, that solution* $-25g_{\star}/1$, one-liter volume bath.	Foor dernsit. MnO2 nracinitate in bath.	2804-135g./1., MgSC4-100g./1., Ma280g-C.25g./1., armonium stannous oxalate solution - 20ml.	Wery good appearing mat plate. Gray deposit. Wery poor black deposit. Smooth tin derosit.	mpsoHyO-40g./l., (4H1)2So135g./l., Me2SO_3-0.25p./l., SnSO1.0g./l., tartaric acid - 25 g./l., hydrolyzed hide glue solution 0.1 g./l., 3-liter volume bath.	Good arpearing may color deposit.	MnSOAHO-50g./l., (NH,)>SO,-135g./l., SnSC,-1.Cp./l., tartaric acid-25g./l., hydrolyzad hide glue solution -0.lg./l., 3-liter volume bath.	Smooth, adherent, metallic mat gray plate. " " " " " " " " " " " " " " " " " " "
Call	4-137 g./		, , ,		SO2-75g./ olution*	1)	7-135g./J		4-135g./1	3.7.2	-135g./1. on -0.1g.	1 0 0 0 1 1
1.5	OSc (MH)	1.16		C. 37	2	• •		Heavy Heavy	QSC(7HA)	26237	(XH ₄) ₂ SO ₄ ue solutí	36.7 3.6.4 3.5.8
Analysis of Esposit		Relance	Palance	• •	MnS0g.H20-100g./1., (NHg arrantum stannous oxalate	1 1	MnSO ₂ *H2C=40g./l., (NH _k) 3-liter volume bath.	Yone Trace	. 3-11ter	Belance s	MnSogH20-5cg./l., hydrolyzad hide gl	Balance
Time PH (Min.)	-04-70S	45 66 31.5	గా కి	• <u>ç</u>	-024 • 1820 - mutura	۶ م	SO, • H ₂ C-	15 ± 51	30,4-H20	8658 1368 13	SORH20-	36 37 37 37 37 37 37 37 37 37 37 37 37 37
j	lon .	7.2		7.2	_	0.7		% * ·		88 88 °C		7.88 7.88 7.8
Current Lensity (Amps./Sq.Pt.)	Rath compositi	22 001	* * 9	173	Bath composition:	90I 97	Bath composition:	ž. • ž	Bath composition:	22623	Bath compositions	100 370 340 220 8
Temp.		301.	• • %	100		38		78		3		120 92 92 80=90 95
Rath No.	7 €	• • • •		• •	35	¥.	¥	4	394	36****	VE7	¥
Test		50.72-29B 29G 30≜ 31≜	75. E.	33.3		5022 -354 -358		5022-364 -368 -360 -360		2023-7CF 717 708 717 708 708 708 708 708 708 708 708 708 70		487 487 477 477 497 497 497

* Ammonium stannous oxalate solution: Composition and details of make-use 50g. SmCl2-28g0 dissolved in HCl solution. Stannous oxalate precipitetal by add dried. A mixture composed of 50 g, dried stannous oxalate, for g. (NH4)26g12-8g0 dissolved in HQU and 15g. High and dried. A mixture composed of 50 ml, of a hydrolyzed hide glue solution prepared by boiling 2g, hide glue in 300 ml, HgC for a hours.

Current Density: 40 ASF

Volts: 3.5

Temperature: 90°F.

Pyrophosphate Type

Solution A. HnSO4. 400 g./1.

Solution B. $K_{l_1}P_2O_7 \cdot 3H_2O$ 800 g./1.

Solution C. N'SO₁.6H₂O 50 g./1.

Plating Solution. Solution A 10 ml.

Water 100 ml.

Solution B 50 ml.

Solution C 5 ml.

Plating Conditions. Anode: Carbon

Cathode: Stainless steel

Current Density: 40 AST

Volts: 3.7

Temperature: 120°F.

pH not measured

Zinc-Tin Alley Plating

This bath has been described by Cuthbertson*. For convenience, the bath formula and plating conditions are given here. In addition, several necessary precautions are mentioned.

^{*}J. Electrochem. Soc. 94, 73 (1948).

Zinc-Tin Alloy-Plating Solution

Tin (as sodium stannate) $30 g_{\bullet}/1_{\bullet}$

Zinc (as zinc cyanide) 2.5 g./l.

Sedium hydroxide (free) 4-6 g./1.

Total cyanide* 25-28 g./l.

Free sodium cyanide 17.5 6./1.

Temperature: 140°F.

Anodes: Cast 20% zinc - 80% tin alloy.

Current Density: 25 ASF

Note: Migh-purity sodium stannate must be used. For commercial units, a special grade is procurable from Metal and Thermit Corp.,

Rahway, N. J. For experimental solutions, the C. P. stannate made by
the J. T. Baker Chemical Co., Phillipsburg, N. J., is suitable.

The bath should be made up as follows: fill the container to two-thirds of its volume with water, preferably distilled or softened, and heat to lh0°F. Dissolve sodium cyanide, sodium hydroxide, and zinc cyanide, in that order. Finally add sodium stannate. Analyze the solution and adjust the components.

It is well to hold the bath at 140°F. for 2-3 days before plating.

Literature on the bath car. De obtained from the Tin Research Institute, Inc., 492 ... Dixth Avenue, columbus 1, thic.

expressed as sodius o anido.

Experimental Zinc-Lead Alloy Fluoborate Solution

Solution A: (Concentrate as supplied by General Chemical Co.)

 $2n(\partial P_h)_2$

50.45% (by weight)

Free H₃BO₃ 3.54%

Solution B: (Concentrate as supplied by General Chemical Co.)

 $Fb(BF_{l_1})_2$

50% (by weight)

Free HBF

0.7%

Free H₃BO₃

4.0%

Solution 4557 - 90A

Solution A

100 .nl.

Solution B

10 ml.

Hide Glue (40 g./1.) 2 ml.

Dilute to 400 ml.

Temperature: 80° - 120°F.

Current Density:

10 - 40 ASF

pH:

0.0 (paper)

Results: Spongy deposit containing only lead.

Experimental Zinc-Lead Alloy Zincate-Plumbite Solution

Zincate Stock Solution

2nOl₂ 75 0./1.

NaOH 255 <./l>

Rochelle Salt 35 ../1.

Zincate-Plumbite Solution

Zincate Stock Solution 400 ml.

 $Pb(OH)(C_2H_3O_2)_3$ 1 g.

RH 774* 0.5 ml.

Temperature: 74°F.

Current Density: 10 ASF

Result: Spongy deposit containing lead only.

Zinc-Lead-Plating Solution

ZnCl₂ 1000 g.

H₂O 500 G.

PbCl₂ 20 &.

Temperature: 170°F.

Current Densities: 300 Table ?3

*nodes: Platinum

^{*}E. I. du Pont de Nemours Co., Wilmington, Del.

TABLE 23. PRELIMINAPY EXPERIMENTS ON THE CODEPOSITION OF ZING AND LEAD

Specimen	Temp.	Temp. C.P. (SE)	C. I. (, SF)	Time (Mins.)	Time (Mins.) Agitation	Feight of Coating (Grems)	\:\marks
5661 - 114 170 0.15 10.	170	0.15	10.7	10	.9	0.095	Deposit is dark, spongy, tread, and non-adherent.
- 118	170	0.034	5.4	07	Ş	0.083	Same as 11A but less treeting and better adherence. 94.9% Pb.
• 11 0	170	0.14	٠	&	Yes.	0.081	Crystalline deposit, somswhat treed, but not spongy. Loosely adherent. 97.6% Ph.
- 11C	170	0.036	1.25	&	* n 0 X	990.0	Fine crystalline denosit. Less trued than llC. Loosely adherent. 85.4% Pb. A subsequent test showed that all the lead was not precipit tel.

* "ork-rod agitation, 1-1/4-inch atroke, 64 strokes/min.

In preparing the zinc-lead chloride solution, the lead chloride was not so readily soluble as it was in lithium chloride solution.

It was necessary to keep the solution hot in order to prevent precipitation. It may be that the material which precipitates when the solution cools is not pure lead chloride, but is a complex such as ZnPbCl).

Cadmium-Silver Plating

Cd 0	32 5./1.
AgCN	2.1 %./1.
NaCN	83 8./1.
на ₂ со ₃	10 g./1.
NH40H(28 %)	2 ml./1.
Free sodium cyanide	32 ₆ ./1.
ries soulum cyanida)2 60/10
Temperature:	90°F.
-	
Temperature:	90 ° F•
Temperature: Current Density:	90°F. 21 ASF

Iron-Chromium Alloy Plating

Analysis of Deposit: 7.4% silver

A complete description of the process for plating ironchromium alloys will be found in the Final Technical Report entitled
"A Research Investigation of Possibilities for Obtaining Hot-Hard
Electrodeposited Chromium or Chromium-Base Alloys for Cannon" (restricted).
This work was done for the Army Ordnance Department under Contract //33019-0AD-6397.

Zinc-Nickel ("Corronized") Coatings

Panels coated with several zinc-nickel alloys were supplied free of charge by the Standard Steel Spring Company, Coraopolis, Pa.

Nitriding of the Steel Panels

The 1-inch by 4-inch SAE 4130 panels were placed in a tubo furnace, ammonia was passed through the furnace, and the temperature was raised to 975°F. This temperature was maintained for four hours. The specimens were then cooled in the furnace in the ammonia atmosphere. The surfaces had the dull-gray appearance characteristic of a nitrided surface. Scratch testing showed the surfaces to have been hardened.

Preparation of Four-Inch by Six-Inch Steel Panels

The SAE 4130 steel used for these panels measured 4 inches by 18 inches by 1/32 inch as received. Before cutting to the desired size of 4 by 6 inches, the steel was cleaned and polished. The larger size permitted easier polishing.

The panels were cleaned in a hot, alkaline, soak cleaner. They were then polished on 240-grit, substantially new, emery belts.

The final finish was with a sisal buff (Tampico wheel). This resulted in a finish about equivalent to a 300 grit. The panels were then cut to the 4-inch by 6-inch size, care being taken not to mar the surfaces. The panels were stored under kerosene until ready to plate.

Description of Plating Racks for Four-Inch by Six-Inch Panels

The so-called "robber" was formed from 1/8-inch by 1-inch hot-rolled, plain-carbon steel. The robber was bent into a rectangular frame measuring $6\frac{1}{2}$ inches by $4\frac{1}{2}$ inches, inside dimensions. The two ends of the frame were welded together. The steel panel is supported within this frame by three contact points. Two of these are located on the inside of the lower $4\frac{1}{2}$ -inch section and are rigid. The third is a spring clip located at the upper $4\frac{1}{2}$ -inch section. A rod is brazed, end on, to the outside of the upper $4\frac{1}{2}$ -inch section. The rack is suspended in the bath by this rod. Figure 7 is a photograph of the plating rack, with a 4-inch x 6-inch panel in place.

A slight modification of the rack was necessary in order to get good distribution when plating manganese. The one-inch-wide strip was narrowed to three-quarters inch, and four quarter-inch holes were drilled in the top strip to allow the gas to escape.

The plating solutions and finishing sequences used in preparing the outdoor panels have been described earlier in this section.

Three thicknesses, O.1 mil., O.3 mil., and O.5 mil., were prepared for each type of coating and four panels for each thickness. The Magne-Gage was used for determining thickness. A tolerance of ±10%, relative to the nominal thicknesses given above was allowed. The magnets that were available were calibrated for man, anese plate.

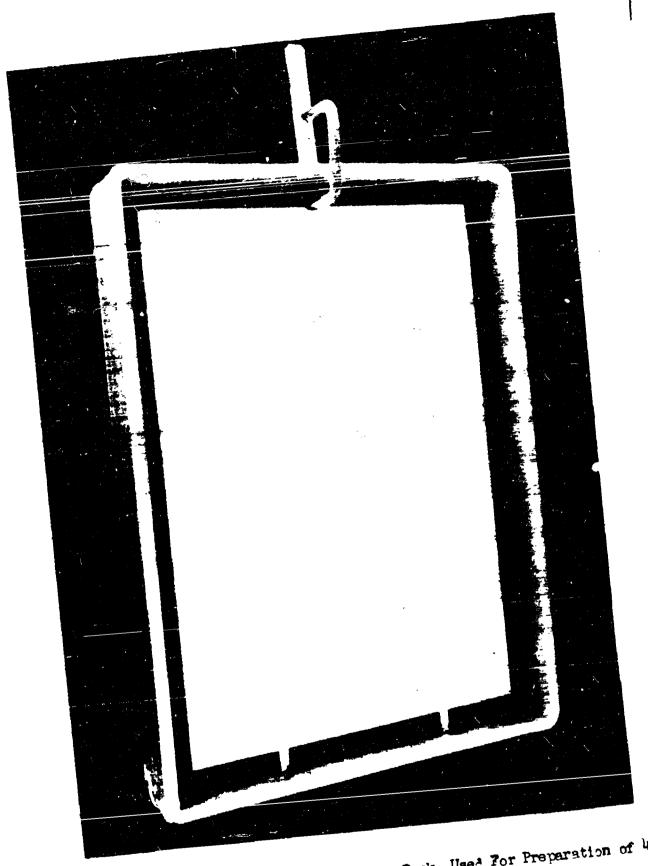


Figure 7. "Robber" Type Plating Rack, Use For Preparation of L. Inch x 6-Inch OutAgor Exposure Panels.

APPENDIX II

This appendix contains tabulated data on the "wet-dry" tests, and the X-ray diffraction photograms.

TABLE 24. DETAILED RESTITE OF WHIT-DIET EXPOSURE TEST

7779 0.417.92	Composition (Veight f)	Speciaen	Coating Thickness (Mils)	Seratehad	Cycles to Total	Total	nerions to essente the fact.
(1840 54 1)	34 880.º	2875-60C1	:	:	:	100	
		60C2	:	:	;	300	
	1.04.8 Ag	(40B)	i	:	:	100	
		60B3	:	:	ı	8	Med. grt. 1396 messuret orts were usede on their stockers. See Teble 1.
	1.24\$ Ag	6041	:	ł	;	100	
		6042	:	•	;	90	
Care Care	D) FOUT	2874-50A	;	:	i	ğ	
		3180-19	:	i	;	5	
	7.35% AB	3363-934	62.0	2	84	٤	of rust plus wary small amount of white crree or areasy.
		3347-436	6.75	Yes	~	•	lof rust. Two-thinds of the risting was along in constaine.
		376-4-920	6.25	ş	~	•	Less than 2f rust, plus small amount of wolth corporation province.
		336 !-93F	6,25	Top	~	•	10% rulet. One-half the runting was along the cornores.
100 mg/m	10% G	89	۲.3	. ₽	No rust	•	
to the rain		3	0.3	≗	•-	•	One rust spot. Less than 1%.
Mr. * Sn overlay		345	^.26 Mm • 406 Sm	Of Sn No	No mist	•	Less manganese corresion products than with the presences. We take that
		₩	ռ. 26 հետ • . 03 Տո	na Sn Mo	Ditto	•	Not quite as gnod as *86% or -80% but thing than the manage.
		980	0.36 MB CA Sh	of Sn ₹o	•	•	Series as with while.

TABLE 25. DETAILED REQUITS OF "WET-DRY" EXFOSURE TEST

Tyne	Currention (Weight 1)	Specimen	Coating Thickness (Mile)	Scratched	Cycles To First Rust	Progress of Rusting After Initial Appearance	Totel Cycles	Final Apparance of Speimen
7d - Sn (11ffueton)	0 % - 0\$	3393-606	67.0	ş		Very Slow	1	3 small rust areas.
	Ditto	-€65F	ر.43	Tes	10	Very Slow	117	Slight rusting in scratches near intersection.
	•	-640	0.35	ş	×	Ditto	134	2 very small rust spots.
	•	199-	o.3	Yes	90	8	1%	Fusting in scratches 50% more than 3393-45P.
'd = Sn Flated From	₩ - ¥	135-6618	50.0	Yes	~	Rapid	*	90% of surface rusted.
Muchinate Schutton)	Ditto	-, -,	0.08	2	10	Repid	76	Sing of murface runted.
	•	11 Y	6. 0	9	Did Not Rust	ļ	134	Wo rust, Gosting slightly dorber then criginally.
	•	#94-	۰.15	Yes	25	Slow	13%	3 to 5" rust along scretches.
7n - Ag (fiffueton)	23-25% Ap	V5465.7	£.°	2	7	Very Rapid	78	BC covered with heavy rust.
(Silver Flated Figure)	Ditto	45	6.3	Tee	rv.	Ditto	200	75% covered with heavy rust.
	•	مرية ر	0.3	Yes	7	•	%	Ditto
		15	Ǖ3	ş	-4	•	#	65% covered with heavy rust.
2n - Ag (Fifueson) (7freson)	23-25# AR	- 08₽	٠ <u>٠</u> ٥	2	~	•	*	80% covered with heavy rust.
() Company of the co	51.440	3 do 5	0.3	¥	7	•	*	516
Wn - Sn (Diffuelon) (Wengenes: Flated First)	42% Sn	98.	6.3	Ş	22	Slow	13%	15% from rust. 10% no corrosion. 75% medium manganese corrosion products.
	•	-465	0.3	.	Fild Not Rust		13%	10% no corrosion. 90% light to medium mangenese corrosion producis.
	=	-461	د.ع	Ç.	N	Slow	134	SOM from rust. 10% no corresion. 40% mentus manganese corresion products.

TABLE 25. (Continued)

Type Composition (Fellow) (Tiffusion) (Mangerese Plated Piret)				`.				
- Sr iffusion) angerese Plated First)	Composition (Feight 9)	Specimen 1	Conting Thickness (Mile)	The state of the s	Cycles to First Bout	Cycles To Progress of Rusting Exect Bust. After Initial Arrestance.	Total	Pinal Appearince
	us X7	4557-84G	0.3	*	300	Slow	134	\$% iron rust, low no cerosicu. 85% medium mange, ie cerosicu products.
	:	E	0.3	£	No Iron Mast	1	13%	<pre>abtire surface covered with meating to heavy brown mangemene-type corrosics products.</pre>
•	: : :	Ş€-	0.3	2	No Iron Rest	1	13%	Entire surface covered with medium to heavy brown mangements or correction products.
				.^_				Motes The surfaces of these specimens were completely control with brown corresion products after two cycles.
· .	•	-77A	0.3	2	300	Slow	1%	Mits posidery correcton preducts covering 90% of surface. 4% . f
•	:	8 %-	0.3	£	£	Slow	134	White powdery correcton producing covering 95% of surface, but more builty than 4557-7PA. 197 of surface shows rust.
		4 6€-	6.0	ē	No Iron Rust	!	134	90% of surface covered with 21 y green-brums, compact extraction product which appears to outlingrains.
í	;	86%	0.3	<u>2</u>	No Iron Rust	•	134	5% of surface as 4557-744.

TABLE 26. DETAILED RESULTS OF WHIT-DRYM EXICOSURE TEST

Convertion (weight #)		Specimer	Costing Thickness (Wile)	Scretched	Cycles to First Rust	Progress of Pusting After Initial Appearance	Total Cycles	Pinel Apropaganta of Specimen
•);	.s 25	187-225	0.3	Ş	æ	Slow	No.	About 30 rust spots covering 4 - 10% of total area. Hedium white corroe on products.
, ,	ر.	187 -	•	£	12	Very slow	128	D1 * ta)
7.55 N3	 Z	-48	•	ş	77	Slow	<u> </u>	Aff rust & Some white correcton readuries.
ik \$5°41	; }	.194-		Yes	<i>e</i>	Slow	7%	Ditto
\$h \$5° 4.	44	187-	•	£	12	Slow A	*	
77.55 M	ž	1 8 7-	•	Yes	Q U	S]ow	136	20% ruse. Some milte corrosion products.
1.9% Ist	전	787-	•	£	7	Rapid	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	net.
259 N.	닭	1347-	*	Yes		Wery rapid	80	MOS rust.
15% N4	.	-78¢	•	ž	160	Rapid	8 x	607 runt.
. 5% 83	7	187-		Yes	1	Ranid	82	60% rust.
te te ty	و	-43E	•	2	` -	Very Yest	\$	RO4 heavy rust.
258 AP	۵	×7-	*** =	۶		Farth	œ.	01100
25% AR	96	民**	•	£	1	Renid	%	
25% Ag	90	1£7-	•	£		Repid	. 6 0	
100% Zn		4557-788	•	٩	 9	Slow	, Z	3. Tust. Balanca of anem covered aith white corresion exeducts
100f h	'n	-787	•	ž	. 9	Slow	8	Ditto
170% Cd	8	ķ	•	£	Did not rust	2: 1st	761	to rust. Siight discoluration,
170% Cd	3	707-	•	` 2	Ditto	1	184 184	- Ditto

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	X	es Time Asperance of Speciesn		,	50% rust 60% rúst	15 rust. Blue-gray/Drown access	Light gray snots, probably sinc correston products, products, distributed evenly over surface, correston products more adherent and less bulky than those of pure mangeness and non-		adherent then those from mire menganess. Shrust, otherwise same as other	Ver. such like nure mangenese, but not so dark. Corresion products are powdery and non-	Possibly 5% scattered rust. Color like rure	508 Tust
	Total	9	র	8 5	র	128		128	128	2	128	র
	Progress of Rusting After	Apitial Appearance Rapid		• •	•	. S) or			•	•	童 건 ^편	Repid
	Grales to	2	~	F4 F4	۱ ۲	3 811		9 <i>c</i>	118	Coestionable	Questionsblo	CV.
16.7	Soratehad	e.		है है	<u>2</u> 2	ž	•	£	2 ;		2 2 ,	ę
	Michael Michael	ú	, * •	•	• •	٠		•		•	•	
	Specimen	74E7-12E5	-4361	Alex.	36C -	54.86-26 2		- 34B	37.	.	5351-358	
	Corrosition (Weight f)	25% Ag 🔆	0116		,	50% Wh	,		3, 5, E E	\$0 %	95% Cr 53	
•	Souting	in-AR (Diffused, ** ** ** property (inet)	Eltte .	" // // // // // // // // // // // // //	'uplem conting. 'no on outeide)	Wa-2s' (Diffied that)	Ditte	ė	· #	Ma-Zn (Diffused		

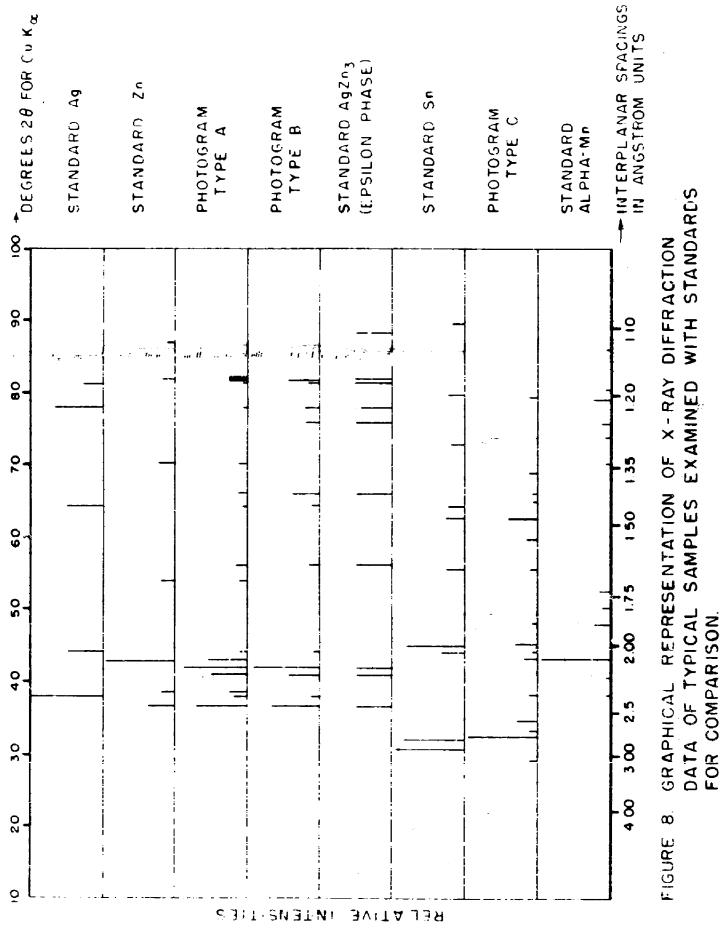
	Final Appearance of Specimen 50% rust 40% rust 50% rust 50% rust	
#.	Total 22 22 24 24 24 24 24 24 24 24 24 24 24 2	
	Progress of Rusting After Hitfal Apror renes	
	Cycles to First Bust 2 2 2 2 2 4 4 4 4 4 4 4 4 4 4 4 4 4 4	
g	Feratebade	~ : g
Continue	Thickness (Mil.) 0.3	a thougher
'Abl& 26. (Continued)	Specimen Thickness Number (Mil.) 5351-35C 0.3 -35E -35G -35G -34B -486-99A -99C -99C	1 a hydroge
	f. con trick the second	Town L. 1
	The Contost Fergett Fe	

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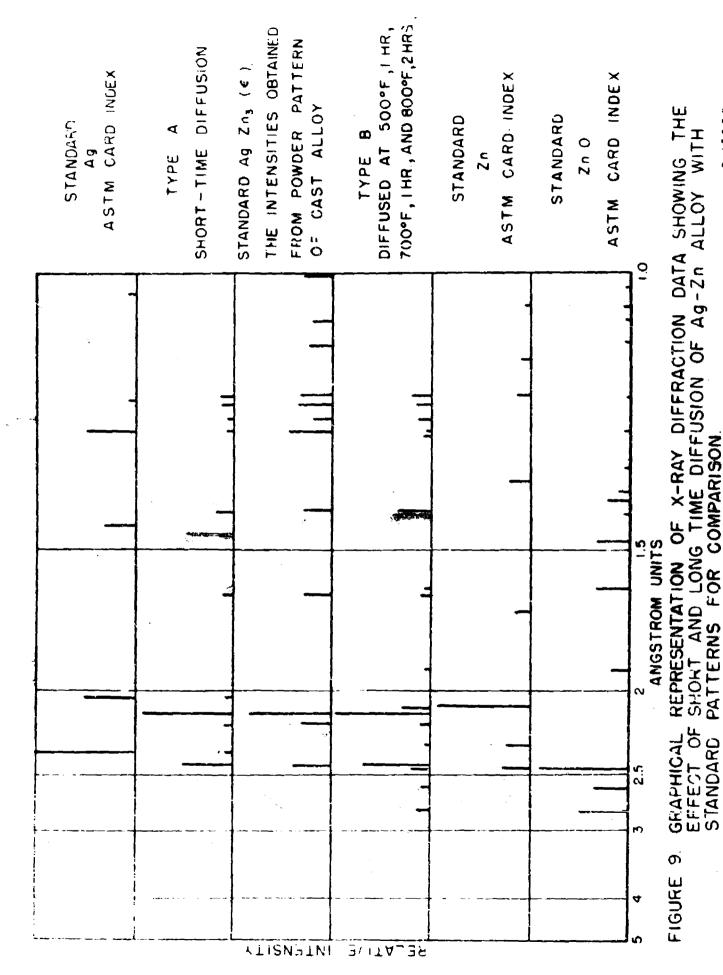
TABLE 27. DETAILED RESULTS OF *PET-DAY" EXPOSURE TEST

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1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1						Rust spots less wishing at 24 cycles. We must wisher at 24 cycles. Resonesting at 36 cycles.		Rust stots not visible at 14 cycles. At 24 cycles 5 rust.									
Index	365	350	1370	1191	719	830	1528	978	067	417	6.17	÷47	73	6c.7	777	197	
Cycles to 50% Rust	3	8	212	212	138	350	Ower 222	164	22	38	*	87	78	\$	83	78	5
Coc. Co.	•	•	*	C+	~	Ø	(£) 9	•	×	., R	07	*	8	8	55	2	,
Scratched	₽	<u>2</u>	£	£	Ĭo.	Yes	ş	æ	ž.	₽	ž	Ş.	Tes	2	Tos	۶	
Coating Thickness (Ells)	0.3	Ditto	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Speciam Bunber	394-9875	Q9 2	728	33 39 39	16r	76G	<u>.</u> 7′	746	5351-538	5.37	5.6	538	534	538	3,5	5	
Commosition (Weight 4)	1			# 105		2	755	:	100% sinc				100f aine				
0 € + 4 € €		(Diffused)							2 ca nitridad	Btag			aleta ec ez	ater1			



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0-15962

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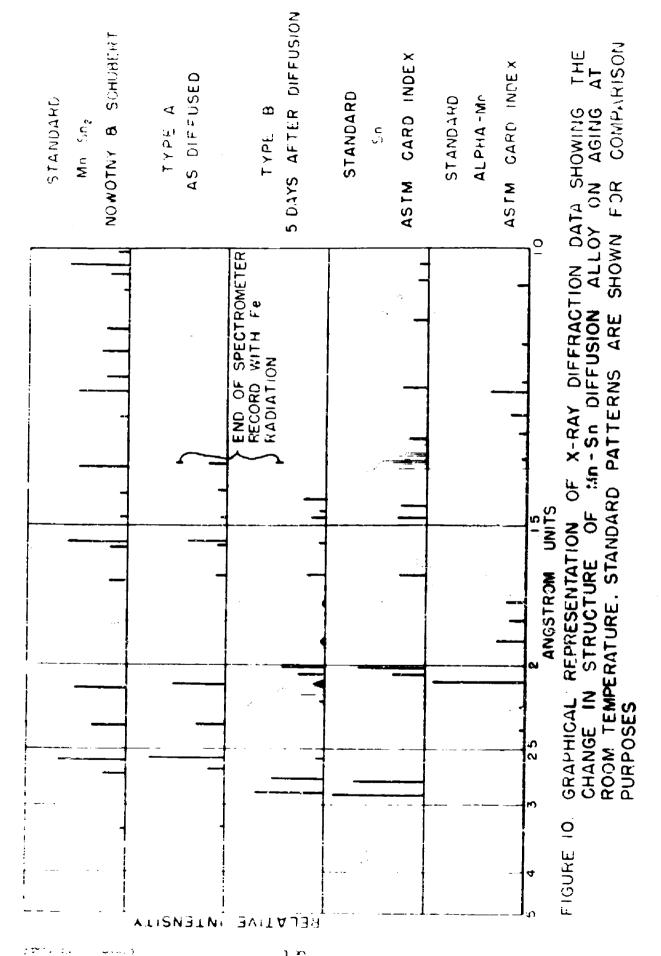


TABLE 28. FOTEUTIAL-TIME DATA FOR SEVERAL DIFFUSION ALLOYS IN THREE FER CENT SODIUM CHLORIDE SOLUTION AT 90°F. SATURATED-CALOREL COLLE. WILLIES IN VOITS.

	Volts* at Elapsed Time of:						
Specimen Number	l Tin,	30 ilin.	60 Min.	120 Lin.	150 !!in,	18C Min.	360 Min.
4557-72B Zn-ag (diffused) approx. 25% Ag		1.038	1.043	1.047	-	1.049	1.050
4557-76A ⁽¹⁾ Cd-Sn(diffused)		0.740	0.747	0.753	-	6.755	0.756
4557-76B ⁽²⁾ C d- Sn (codeposited,	0.729	.7.1	0.728	0.732	•	0.733	0.730
4557-84A Mn-Sn(diffusol)	1 2	1.075	1.020	1.032	1.114	1.133	•
2875-72B SAE 413 0 steel	0,590	0,710	0,707	••	0.707	•	-

^{*} All values are negative.

⁽¹⁾ Specimens received from Air Meterials Laboratory, Mavel Air Materiel Center, Nevy Yard, Philadelphia Fa. Composition approximately 50-50

⁽²⁾ Received from same nource as 4557-76A. Commosition approximately 50-50. Coderosited from fluohorate solution.

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